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(54) Title: DRYING WET FLUOROPOLYMER RESIN AND EXPOSING TO OXYGEN SOURCE TO REDUCE DISCOLORATION

(57) Abstract: Process for reducing thermally induced discoloration of fluoropolymer resin produced by polymerizing fluoromonomer in an aqueous dispersion medium to form aqueous fluoropolymer dispersion and isolating fluoropolymer from said aqueous medium by separating wet fluoropolymer resin from the aqueous medium and drying to produce fluoropolymer resin. The process comprises: exposing the wet fluoropolymer resin to an oxygen source during drying.



**TITLE OF THE INVENTION**

Drying Wet Fluoropolymer Resin and Exposing to Oxygen Source to  
Reduce Discoloration

5

**FIELD OF THE INVENTION**

This invention relates to a process for reducing thermally induced discoloration of fluoropolymer resin.

**BACKGROUND OF THE INVENTION**

10

A typical process for the aqueous dispersion polymerization of fluorinated monomer to produce fluoropolymer includes feeding fluorinated monomer to a heated reactor containing an aqueous medium and adding a free-radical initiator to commence polymerization. A fluorosurfactant is typically employed to stabilize the fluoropolymer particles formed. After  
15 several hours, the feeds are stopped, the reactor is vented and purged with nitrogen, and the raw dispersion in the vessel is transferred to a cooling vessel.

20

The fluoropolymer formed can be isolated from the dispersion to obtain fluoropolymer resin. For example, polytetrafluoroethylene (PTFE) resin referred to as PTFE fine powder is produced by isolating PTFE resin from PTFE dispersion by coagulating the dispersion to separate PTFE from the aqueous medium and then drying. Dispersions of melt-processible fluoropolymers such as copolymers of tetrafluoroethylene and hexafluoropropylene (FEP) and tetrafluoroethylene and perfluoro (alkyl  
25 vinyl ethers) (PFA) useful as molding resins can be similarly coagulated and the coagulated polymer is dried and then used directly in melt-processing operations or melt-processed into a convenient form such as chip or pellet for use in subsequent melt-processing operations.

30

Because of environmental concerns relating to fluorosurfactants, there is interest in using hydrocarbon surfactants in the aqueous polymerization medium in place of a portion of or all of the fluorosurfactant. However, when fluoropolymer dispersion is formed which contains hydrocarbon surfactant and is subsequently isolated to obtain fluoropolymer resin, the fluoropolymer resin is prone to thermally induced

discoloration. By thermally induced discoloration is meant that undesirable color forms or increases in the fluoropolymer resin upon heating. It is usually desirable for fluoropolymer resin to be clear or white in color and, in resin prone to thermally induced discoloration, a gray or brown color, sometimes quite dark forms upon heating. For example, if PTFE fine power produced from dispersion containing the hydrocarbon surfactant sodium dodecyl sulfate (SDS) is converted into paste-extruded shapes or films and subsequently sintered, an undesirable gray or brown color will typically arise. Color formation upon sintering in PTFE produced from dispersion containing the hydrocarbon surfactant SDS has been described in Example VI of U.S. Patent 3,391,099 to Punderson. Similarly, when melt-processible fluoropolymers such as FEP or PFA are produced from dispersions containing hydrocarbon surfactant such as SDS, undesirable color typically occurs when the fluoropolymer is first melt-processed, for example, when melt processed into a convenient form for subsequent use such as chip or pellet.

### **SUMMARY OF THE INVENTION**

The invention provides a process for reducing thermally induced discoloration of fluoropolymer resin produced by polymerizing fluoromonomer in an aqueous dispersion medium to form aqueous fluoropolymer dispersion and isolating fluoropolymer from said aqueous medium by separating wet fluoropolymer resin from the aqueous medium and drying to produce fluoropolymer resin. It has been discovered that thermally induced discoloration of the fluoropolymer resin can be reduced by:

exposing the wet fluoropolymer resin to an oxygen source during drying.

Preferably, the process reduces the thermally induced discoloration by at least about 10% as measured by % change in L\* on the CIELAB color scale.

The process of the invention is useful for fluoropolymer resin which exhibits thermally induced discoloration which ranges from mild to severe. The process of the invention may be employed for fluoropolymer resin

which exhibits thermally induced discoloration prior to treatment which is significantly greater than equivalent fluoropolymer resin of commercial quality manufactured using ammonium perfluorooctanoate fluorosurfactant. The process of the invention is advantageously

- 5 employed when the fluoropolymer resin has an initial thermally induced discoloration value ( $L^*$ ) at least about 4 L units on the CIELAB color scale below the  $L^*$  value of equivalent fluoropolymer resin of commercial quality manufactured using ammonium perfluorooctanoate fluorosurfactant.

- 10 The invention is particularly useful for fluoropolymer resin obtained from aqueous fluoropolymer dispersion made by polymerizing fluoromonomer containing hydrocarbon surfactant which causes thermally induced discoloration, preferably aqueous fluoropolymer dispersion polymerized in the presence of hydrocarbon surfactant.

15 **DETAILED DESCRIPTION OF THE INVENTION**

**Fluoromonomer/Fluoropolymer**

- Fluoropolymer resins are produced by polymerizing fluoromonomer in an aqueous medium to form aqueous fluoropolymer dispersion. The fluoropolymer is made from at least one fluorinated monomer
- 20 (fluoromonomer), i.e., wherein at least one of the monomers contains fluorine, preferably an olefinic monomer with at least one fluorine or a fluoroalkyl group attached to a doubly-bonded carbon. The fluorinated monomer and the fluoropolymer obtained therefrom each preferably contain at least 35 wt% F, preferably at least 50 wt% F and the fluorinated
- 25 monomer is preferably independently selected from the group consisting of tetrafluoroethylene (TFE), hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), trifluoroethylene, hexafluoroisobutylene, perfluoroalkyl ethylene, fluorovinyl ethers, vinyl fluoride (VF), vinylidene fluoride (VF<sub>2</sub>), perfluoro-2,2-dimethyl-1,3-dioxole (PDD), perfluoro-2-
- 30 methylene-4-methyl-1,3-dioxolane (PMD), perfluoro(allyl vinyl ether) and perfluoro(butenyl vinyl ether) and mixtures thereof. A preferred perfluoroalkyl ethylene monomer is perfluorobutyl ethylene (PFBE). Preferred fluorovinyl ethers include perfluoro(alkyl vinyl ether) monomers (PAVE) such as perfluoro(propyl vinyl ether) (PPVE), perfluoro(ethyl vinyl

ether) (PEVE), and perfluoro(methyl vinyl ether) (PMVE). Non-fluorinated olefinic comonomers such as ethylene and propylene can be copolymerized with fluorinated monomers.

Fluorovinyl ethers also include those useful for introducing  
5 functionality into fluoropolymers. These include  $\text{CF}_2=\text{CF}-(\text{O}-\text{CF}_2\text{CFR}_f)_a-\text{O}-\text{CF}_2\text{CFR}'_f\text{SO}_2\text{F}$ , wherein  $\text{R}_f$  and  $\text{R}'_f$  are independently selected from F, Cl or a perfluorinated alkyl group having 1 to 10 carbon atoms,  $a = 0, 1$  or 2. Polymers of this type are disclosed in U.S. Patent No. 3,282,875 ( $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ , perfluoro(3,6-dioxa-4-methyl-  
10 7-octenesulfonyl fluoride)), and in U.S. Patent Nos. 4,358,545 and 4,940,525 ( $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2\text{CF}_2\text{SO}_2\text{F}$ ). Another example is  $\text{CF}_2=\text{CF}-\text{O}-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2\text{CF}_2\text{CO}_2\text{CH}_3$ , methyl ester of perfluoro(4,7-dioxa-5-methyl-8-nonenecarboxylic acid), disclosed in U.S. Patent No. 4,552,631. Similar fluorovinyl ethers with functionality of nitrile, cyanate, carbamate,  
15 and phosphonic acid are disclosed in U.S. Patent Nos. 5,637,748; 6,300,445; and 6,177,196.

A preferred class of fluoropolymers useful for reducing thermally induced discoloration is perfluoropolymers in which the monovalent substituents on the carbon atoms forming the chain or backbone of the  
20 polymer are all fluorine atoms, with the possible exception of comonomer, end groups, or pendant group structure. Preferably the comonomer, end group, or pendant group structure will impart no more than 2 wt% C-H moiety, more preferably no greater than 1 wt% C-H moiety, with respect to the total weight of the perfluoropolymer. Preferably, the hydrogen content,  
25 if any, of the perfluoropolymer is no greater than 0.2 wt%, based on the total weight of the perfluoropolymer.

The process of the present invention is also useful in reducing thermally induced discoloration of low molecular weight PTFE, which is commonly known as PTFE micropowder, so as to distinguish from the  
30 PTFE described above. The molecular weight of PTFE micropowder is low relative to PTFE, i.e. the molecular weight ( $M_n$ ) is generally in the range of  $10^4$  to  $10^5$ . The result of this lower molecular weight of PTFE micropowder is that it has fluidity in the molten state, in contrast to PTFE which is not melt flowable. PTFE micropowder has melt flowability, which

can be characterized by a melt flow rate (MFR) of at least 0.01 g/10 min, preferably at least 0.1 g/10 min and more preferably at least 5 g/10 min, and still more preferably at least 10 g/10 min., as measured in accordance with ASTM D 1238, at 372°C using a 5 kg weight on the molten polymer.

5           The invention is especially useful for reducing thermally induced discoloration of melt-processible fluoropolymers that are also melt-fabricable. Melt-processible means that the fluoropolymer can be processed in the molten state, i.e., fabricated from the melt using conventional processing equipment such as extruders and injection  
10   molding machines, into shaped articles such as films, fibers, and tubes. Melt-fabricable means that the resultant fabricated articles exhibit sufficient strength and toughness to be useful for their intended purpose. This sufficient strength may be characterized by the fluoropolymer by itself exhibiting an MIT Flex Life of at least 1000 cycles, preferably at least 2000  
15   cycles, measured as disclosed in U.S. Patent Number 5,703,185. The strength of the fluoropolymer is indicated by it not being brittle.

Examples of such melt-processible fluoropolymers include homopolymers such as polychlorotrifluoroethylene and polyvinylidene fluoride (PVDF) or copolymers of tetrafluoroethylene (TFE) and at least  
20   one fluorinated copolymerizable monomer (comonomer) present in the polymer usually in sufficient amount to reduce the melting point of the copolymer substantially below that of PTFE, e.g., to a melting temperature no greater than 315°C.

A melt-processible TFE copolymer typically incorporates an amount  
25   of comonomer into the copolymer in order to provide a copolymer which has a melt flow rate (MFR) of 0.1 to 200 g/10 min as measured according to ASTM D-1238 using a 5 kg weight on the molten polymer and the melt temperature which is standard for the specific copolymer. MFR will preferably range from 1 to 100 g/10 min, most preferably about 1 to about  
30   50 g/10 min. Additional melt-processible fluoropolymers are the copolymers of ethylene (E) or propylene (P) with TFE or CTFE, notably ETFE and ECTFE .

A preferred melt-processible copolymer for use in the practice of the present invention comprises at least 40-99 mol% tetrafluoroethylene

units and 1-60 mol% of at least one other monomer. Additional melt-processible copolymers are those containing 60-99 mol% PTFE units and 1-40 mol% of at least one other monomer. Preferred comonomers with TFE to form perfluoropolymers are perfluoromonomers, preferably

5 perfluoroolefin having 3 to 8 carbon atoms, such as hexafluoropropylene (HFP), and/or perfluoro(alkyl vinyl ether) (PAVE) in which the linear or branched alkyl group contains 1 to 5 carbon atoms. Preferred PAVE monomers are those in which the alkyl group contains 1, 2, 3 or 4 carbon atoms, and the copolymer can be made using several PAVE monomers.

10 Preferred TFE copolymers include FEP (TFE/HFP copolymer), PFA (TFE/PAVE copolymer), TFE/HFP/PAVE wherein PAVE is PEVE and/or PPVE, MFA (TFE/PMVE/PAVE wherein the alkyl group of PAVE has at least two carbon atoms) and THV (TFE/HFP/VF<sub>2</sub>).

All these melt-processible fluoropolymers can be characterized by

15 MFR as recited above for the melt-processible TFE copolymers, i.e. by the procedure of ASTM 1238 using standard conditions for the particular polymer, including a 5 kg weight on the molten polymer in the plastometer for the MFR determination of PFA and FEP

Further useful polymers are film forming polymers of polyvinylidene fluoride (PVDF) and copolymers of vinylidene fluoride as well as polyvinyl fluoride (PVF) and copolymers of vinyl fluoride.

20

The invention is also useful when reducing thermally induced discoloration of fluorocarbon elastomers (fluoroelastomers). These elastomers typically have a glass transition temperature below 25°C and

25 exhibit little or no crystallinity at room temperature and little or no melting temperature. Fluoroelastomer made by the process of this invention typically are copolymers containing 25 to 75 wt%, based on total weight of the fluoroelastomer, of copolymerized units of a first fluorinated monomer which may be vinylidene fluoride (VF<sub>2</sub>) or tetrafluoroethylene (TFE). The

30 remaining units in the fluoroelastomers are comprised of one or more additional copolymerized monomers, different from the first monomer, selected from the group consisting of fluorinated monomers, hydrocarbon olefins and mixtures thereof. Fluoroelastomers may also, optionally, comprise units of one or more cure site monomers. When present,

copolymerized cure site monomers are typically at a level of 0.05 to 7 wt%, based on total weight of fluorocarbon elastomer. Examples of suitable cure site monomers include: i) bromine -, iodine -, or chlorine - containing fluorinated olefins or fluorinated vinyl ethers; ii) nitrile group-  
5 containing fluorinated olefins or fluorinated vinyl ethers; iii) perfluoro(2-phenoxypropyl vinyl ether); and iv) non-conjugated dienes.

Preferred TFE based fluoroelastomer copolymers include TFE/PMVE, TFE/PMVE/E, TFE/P and TFE/P/VF<sub>2</sub>. Preferred VF<sub>2</sub> based fluorocarbon elastomer copolymers include VF<sub>2</sub>/HFP, VF<sub>2</sub>/HFP/TFE, and  
10 VF<sub>2</sub>/PMVE/TFE. Any of these elastomer copolymers may further comprise units of cure site monomer.

### **Hydrocarbon Surfactants**

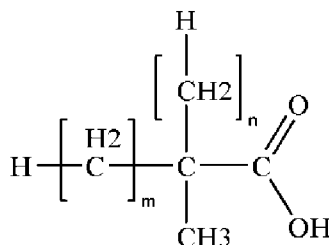
In one embodiment of the present invention, the aqueous  
15 fluoropolymer dispersion medium used to form fluoropolymer resin contains hydrocarbon surfactant which causes thermally induced discoloration in the resin when the fluoropolymer resin is isolated and heated. The hydrocarbon surfactant is a compound that has hydrophobic and hydrophilic moieties, which enables it to disperse and stabilize  
20 hydrophobic fluoropolymer particles in an aqueous medium. The hydrocarbon surfactant is preferably an anionic surfactant. An anionic surfactant has a negatively charged hydrophilic portion such as a carboxylate, sulfonate, or sulfate salt and a long chain hydrocarbon portion, such as alkyl as the hydrophobic portion. Hydrocarbon  
25 surfactants often serve to stabilize polymer particles by coating the particles with the hydrophobic portion of the surfactant oriented towards the particle and the hydrophilic portion of the surfactant in the water phase. The anionic surfactant adds to this stabilization because it is charged and provides repulsion of the electrical charges between polymer  
30 particles. Surfactants typically reduce surface tension of the aqueous medium containing the surfactant significantly.

One example anionic hydrocarbon surfactant is the highly branched C10 tertiary carboxylic acid supplied as Versatic® 10 by Resolution Performance Products.



Versatic® 10

Neodecanoic acid (n+m=7)



5

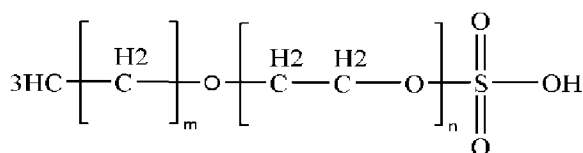
Another useful anionic hydrocarbon surfactant is the sodium linear alkyl polyether sulfonates supplied as the Avanel® S series by BASF. The ethylene oxide chain provides nonionic characteristics to the surfactant and the sulfonate groups provide certain anionic characteristics.

10

Avanel®

S-70 (n=7, m=11-14)

S-74 (n=3, m=8)



Another group of hydrocarbon surfactants are those anionic

15 surfactants represented by the formula R-L-M wherein R is preferably a straight chain alkyl group containing from 6 to 17 carbon atoms, L is selected from the group consisting of  $-\text{ArSO}_3^-$ ,  $-\text{SO}_3^-$ ,  $-\text{SO}_4^-$ ,  $-\text{PO}_3^-$ ,  $-\text{PO}_4^-$  and  $-\text{COO}^-$ , and M is a univalent cation, preferably  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ .  $-\text{ArSO}_3^-$  is aryl sulfonate. Preferred of these surfactants are those

20 represented by the formula  $\text{CH}_3-(\text{CH}_2)_n-\text{L}-\text{M}$ , wherein n is an integer of 6 to 17 and L is selected from  $-\text{SO}_4\text{M}$ ,  $-\text{PO}_3\text{M}$ ,  $-\text{PO}_4\text{M}$ , or  $-\text{COOM}$  and L and M have the same meaning as above. Especially preferred are R-L-M surfactants wherein the R group is an alkyl group having 12 to 16 carbon atoms and wherein L is sulfate, and mixtures thereof. Especially preferred

25 of the R-L-M surfactants is sodium dodecyl sulfate (SDS). For commercial use, SDS (sometimes referred to as sodium lauryl sulfate or SLS), is typically obtained from coconut oil or palm kernel oil feedstocks, and contains predominately sodium dodecyl sulfate but may contain minor quantities of other R-L-M surfactants with differing R groups. "SDS" as

30 used in this application means sodium dodecyl sulfate or surfactant mixtures which are predominantly sodium dodecyl sulphate containing minor quantities of other R-L-M surfactants with differing R groups.

Another example of anionic hydrocarbon surfactant useful in the present invention is the sulfosuccinate surfactant Lankropol® K8300

available from Akzo Nobel Surface Chemistry LLC . The surfactant is reported to be the following:

Butanedioic acid, sulfo-, 4-(1-methyl-2-((1-oxo-9-octadecenyl)amino)ethyl) ester, disodium salt; CAS No.:67815-88-7

- 5 Additional sulfosuccinate hydrocarbon surfactants useful in the present invention are diisodecyl sulfosuccinate, Na salt, available as Emulsogen® SB10 from Clariant, and diisotridecyl sulfosuccinate, Na salt, available as Polirol® TR/LNA from Cesapinia Chemicals.

- Another preferred class of hydrocarbon surfactants is nonionic  
10 surfactants. A nonionic surfactant does not contain a charged group but has a hydrophobic portion that is typically a long chain hydrocarbon. The hydrophilic portion of the nonionic surfactant typically contains water soluble functionality such as a chain of ethylene ether derived from polymerization with ethylene oxide. In the stabilization context, surfactants  
15 stabilize polymer particles by coating the particles with the hydrophobic portion of the surfactant oriented towards the particle and the hydrophilic portion of the surfactant in the water phase.

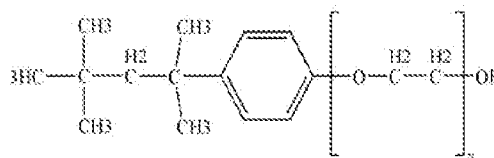
- Nonionic hydrocarbon surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene alkyl esters,  
20 sorbitan alkyl esters, polyoxyethylene sorbitan alkyl esters, glycerol esters, their derivatives and the like. More specifically examples of polyoxyethylene alkyl ethers are polyoxyethylene lauryl ether, polyoxyethylene cetyl ether, polyoxyethylene stearyl ether, polyoxyethylene oleyl ether, polyoxyethylene behenyl ether and the like;  
25 examples of polyoxyethylene alkyl phenyl ethers are polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether and the like; examples of polyoxyethylene alkyl esters are polyethylene glycol monolaurylate, polyethylene glycol monooleate, polyethylene glycol monostearate and the like; examples of sorbitan alkyl esters are  
30 polyoxyethylene sorbitan monolaurylate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate, polyoxyethylene sorbitan monooleate and the like; examples of polyoxyethylene sorbitan alkyl esters are polyoxyethylene sorbitan monolaurylate, polyoxyethylene sorbitan monopalmitate, polyoxyethylene sorbitan monostearate and the

like; and examples of glycerol esters are glycerol monomyristate, glycerol monostearate, glycerol monooleate and the like. Also examples of their derivatives are polyoxyethylene alkyl amine, polyoxyethylene alkyl phenyl-formaldehyde condensate, polyoxyethylene alkyl ether phosphate and the like. Particularly preferable are polyoxyethylene alkyl ethers and polyoxyethylene alkyl esters. Examples of such ethers and esters are those that have an HLB value of 10 to 18. More particularly there are polyoxyethylene lauryl ether (EO: 5 to 20. EO stands for an ethylene oxide unit.), polyethylene glycol monostearate (EO: 10 to 55) and polyethylene glycol monooleate (EO: 6 to 10).

Suitable nonionic hydrocarbon surfactants include octyl phenol ethoxylates such as the Triton® X series supplied by Dow Chemical Company:

Triton®

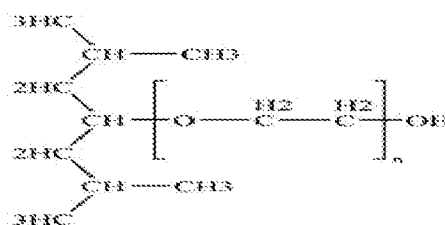
X15 (n~1.5)  
X45 (n~4.5)  
X100 (n~10)



Preferred nonionic hydrocarbon surfactants are branched alcohol ethoxylates such as the Tergitol® 15-S series supplied by Dow Chemical Company and branched secondary alcohol ethoxylates such as the Tergitol® TMN series also supplied by Dow Chemical Company.:

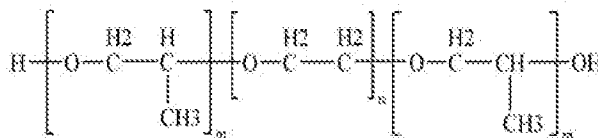
Tergitol®

TMN-6 (n~8)  
TMN-10 (n~11)  
TMN-100 (n~10)



Ethyleneoxide/propylene oxide copolymers such as the Tergitol® L series surfactant supplied by Dow Chemical Company are also useful as nonionic surfactants in this invention.

Yet another useful group of suitable nonionic hydrocarbon surfactants are difunctional block copolymers supplied as Pluronic® R series from BASF, such as:



## Pluronic® R

31R1 (m~26, n~8)

17R2 (m~14, n~9)

10R5 (m~8, n~22)

5

25R4 (m~22, n~23)

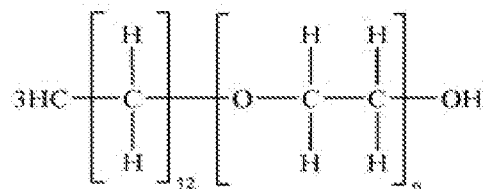
Another group of suitable nonionic hydrocarbon surfactants are tridecyl alcohol alkoxyates supplied as Iconol® TDA series from BASF Corporation.

10 Iconol®

TDA-6 (n=6)

TDA-9 (n=9)

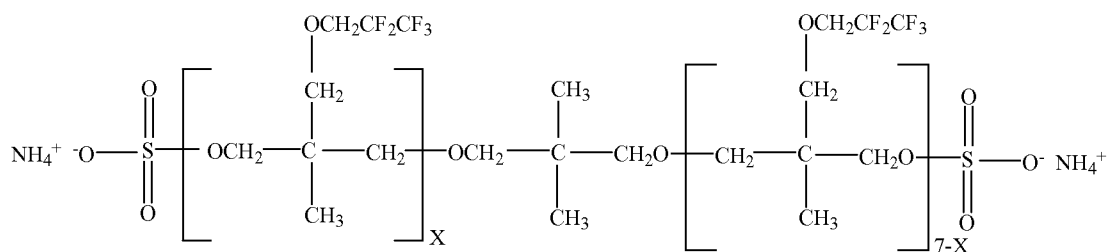
TDA-10 (n=10)



15 In a preferred embodiment, all of the monovalent substituents on the carbon atoms of the hydrocarbon surfactants are hydrogen. The hydrocarbon surfactant is preferably essentially free of halogen substituents, such as fluorine or chlorine. Accordingly, the monovalent substituents, as elements from the Periodic Table, on the carbon atoms of

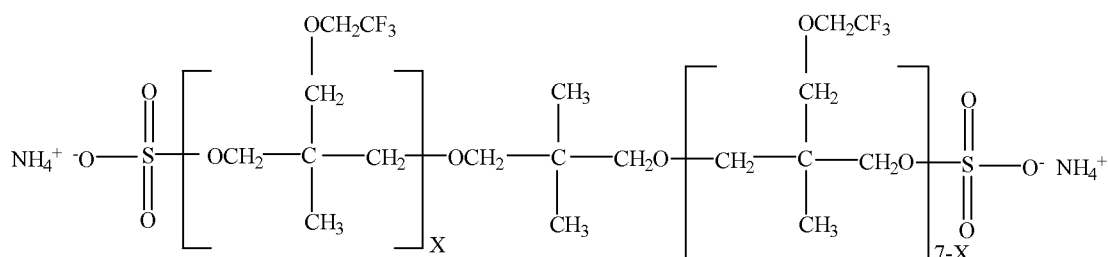
20 the surfactant are at least 75%, preferably at least 85 %, and more preferably at least 95% hydrogen. Most preferably, 100% of the monovalent substituents as elements of the Periodic Table, on the carbon atoms are hydrogen. However, in one embodiment, a number of carbon atoms can contain halogen atoms in a minor amount.

25 Examples of hydrocarbon-containing surfactants useful in the present invention in which only a minor number of monovalent substituents on carbon atoms are fluorine instead of hydrogen are the PolyFox® surfactants available from Omnova Solutions, Inc., described below

**PolyFox™ PF-156A**

MW ~1900, X=1 to7

5

**PolyFox™ PF-136A**

MW~1600, X=1 to 7

10

**Polymerization Process**

For the practice of the present invention, fluoropolymer resin is produced by polymerizing fluoromonomer. Polymerization may be suitably carried out in a pressurized polymerization reactor which produces aqueous fluoropolymer dispersion. A batch or continuous process may be used although batch processes are more common for commercial production. The reactor is preferably equipped with a stirrer for the aqueous medium and a jacket surrounding the reactor so that the reaction temperature may be conveniently controlled by circulation of a controlled temperature heat exchange medium. The aqueous medium is preferably deionized and deaerated water. The temperature of the reactor and thus of the aqueous medium will preferably be from about 25 to about 120°C .

To carry out polymerization, the reactor is typically pressured up with fluoromonomer to increase the reactor internal pressure to operating pressure which is generally in the range of about 30 to about 1000 psig (0.3 to 7.0 MPa). An aqueous solution of free-radical polymerization

initiator can then be pumped into the reactor in sufficient amount to cause kicking off of the polymerization reaction, i.e. commencement of the polymerization reaction. The polymerization initiator employed is preferably a water-soluble free-radical polymerization initiator. For  
5 polymerization of TFE to PTFE, preferred initiator is organic peracid such as disuccinic acid peroxide (DSP), which requires a large amount to cause kickoff, e.g. at least about 200 ppm, together with a highly active initiator, such as inorganic persulfate salt such as ammonium persulfate in a smaller amount. For TFE copolymers such as FEP and PFA, inorganic  
10 persulfate salt such as ammonium persulfate is generally used. The initiator added to cause kickoff can be supplemented by pumping additional initiator solution into the reactor as the polymerization reaction proceeds.

For the production of modified PTFE and TFE copolymers,  
15 relatively inactive fluoromonomer such as hexafluoropropylene (HFP) can already be present in the reactor prior to pressuring up with the more active TFE fluoromonomer. After kickoff, TFE is typically fed into the reactor to maintain the internal pressure of the reactor at the operating pressure. Additional comonomer such as HFP or perfluoro (alkyl vinyl  
20 ether) can be pumped into the reactor if desired. The aqueous medium is typically stirred to obtain a desired polymerization reaction rate and uniform incorporation of comonomer, if present. Chain transfer agents can be introduced into the reactor when molecular weight control is desired.

25 In one embodiment of the present invention, the aqueous fluoropolymer dispersion is polymerized in the presence of hydrocarbon surfactant. Hydrocarbon surfactant is preferably present in the fluoropolymer dispersion because the aqueous fluoropolymer dispersion is polymerized in the presence of hydrocarbon surfactant, i.e., hydrocarbon  
30 surfactant is used as a stabilizing surfactant during polymerization. If desired fluorosurfactant such a fluoroalkane carboxylic acid or salt or fluoroether carboxylic acid or salt may be employed as stabilizing surfactant together with hydrocarbon surfactant and therefore may also present in the aqueous fluoropolymer dispersion produced. Preferably for

the practice of the present invention, the fluoropolymer dispersion is preferably free of halogen-containing surfactant such as fluorosurfactant, i.e., contains less than about 300 ppm, and more preferably less than about 100 ppm, and most preferably less than 50 ppm, or halogen-  
5 containing surfactant.

In a polymerization process employing hydrocarbon surfactant as the stabilizing surfactant, addition of the stabilizing surfactant is preferably delayed until after the kickoff has occurred. The amount of the delay will depend on the surfactant being used and the fluoromonomer being  
10 polymerized. In addition, it is preferably for the hydrocarbon surfactant to be fed into the reactor as the polymerization proceeds, i.e., metered. The amount of hydrocarbon surfactant present in the aqueous fluoropolymer dispersion produced is preferably 10 ppm to about 50,000 ppm, more preferably about 50 ppm to about 10,000 ppm, most preferably about 100  
15 ppm to about 5000 ppm, based on fluoropolymer solids.

If desired, the hydrocarbon surfactant can be passivated prior to, during or after addition to the polymerization reactor. Passivating means to reduce the telogenic behavior of the hydrocarbon-containing surfactant. Passivation may be carried out by reacting said the hydrocarbon-  
20 containing surfactant with an oxidizing agent, preferably hydrogen peroxide or polymerization initiator. Preferably, the passivating of the hydrocarbon-containing surfactant is carried out in the presence of a passivation adjuvant, preferably metal in the form of metal ion, most preferably, ferrous ion or cuprous ion.

25 After completion of the polymerization when the desired amount of dispersed fluoropolymer or solids content has been achieved (typically several hours in a batch process), the feeds are stopped, the reactor is vented, and the raw dispersion of fluoropolymer particles in the reactor is transferred to a cooling or holding vessel.

30 The solids content of the aqueous fluoropolymer dispersion as polymerized produced can range from about 10% by weight to up to about 65 wt% by weight but typically is about 20% by weight to 45% by weight.

Particle size (Dv(50)) of the fluoropolymer particles in the aqueous fluoropolymer dispersion can range from 10 nm to 400 nm, preferably Dv(50) about 100 to about 400 nm.

Isolation of the fluoropolymer includes separation of wet  
5 fluoropolymer resin from the aqueous fluoropolymer dispersion. Separation of the wet fluoropolymer resin from the aqueous fluoropolymer dispersion can be accomplished by a variety of techniques including but not limited to gelation, coagulation, freezing and thawing, and solvent aided pelletization (SAP). When separation of wet fluoropolymer resin is  
10 carried out by coagulation, the as polymerized dispersion may first be diluted from its as polymerized concentration. Stirring is then suitably employed to impart sufficient shear to the dispersion to cause coagulation and thereby produce undispersed fluoropolymer. Salts such as ammonium carbonate can be added to the dispersion to assist with  
15 coagulation if desired. Filtering can be used to remove at least a portion of the aqueous medium from the wet fluoropolymer resin. Separation can be performed by solvent aided pelletization as described in U.S. Patent Number 4,675,380 which produces granulated particles of fluoropolymer.

Isolating the fluoropolymer typically includes drying to remove  
20 aqueous medium which is retained in the fluoropolymer resin. After wet fluoropolymer resin is separated from the dispersion, fluoropolymer resin in wet form can include significant quantities of the aqueous medium, for example, up to 60% by weight. Drying removes essentially all of the aqueous medium to produce fluoropolymer resin in dry form. The wet  
25 fluoropolymer resin may be rinsed if desired and may be pressed to reduce aqueous medium content to reduce the energy and time required for drying.

For melt-processible fluoropolymers, wet fluoropolymer resin is dried and used directly in melt-processing operations or processed into a  
30 convenient form such as chip or pellet for use in subsequent melt-processing operations. Certain grades of PTFE dispersion are made for the production of fine powder. For this use, the dispersion is coagulated, the aqueous medium is removed and the PTFE is dried to produce fine powder. For fine powder, conditions are suitably employed during



isolation which do not adversely affect the properties of the PTFE for end use processing. The shear in the dispersion during stirring is appropriately controlled and temperatures less than 200°C, well below the sintering temperature of PTFE, are employed during drying.

5

### **Reduction of Thermally Induced Discoloration**

To reduce thermally induced discoloration in accordance with the present invention, wet fluoropolymer resin is exposed to an oxygen source during drying. Preferably, the process of the invention reduces the thermally induced discoloration by at least about 10% as measured by % change in L\* on the CIELAB color scale. As discussed in detail in the Test Methods which follow, the % change in L\* of fluoropolymer resin samples is determined using the CIELAB color scale specified by International Commission on Illumination (CIE). More preferably, the process reduces the thermally induced discoloration by at least about 20% as measured by % change in L\*, still more preferably at least about 30%, and most preferably at least about 50%.

The wet fluoropolymer resin for use in the practice of the invention is preferably undispersed fluoropolymer as separated from the dispersion.

Any of various equipment known for use in drying fluoropolymer resin can be used for the practice of the invention. In such equipment a heated drying gas, typically air, is used as a heat transfer medium to heat the fluoropolymer resin and to convey away water vapor and chemicals removed from the fluoropolymer resin during drying. Preferably in accordance with the present invention, the drying gas employed is the oxygen source or includes the oxygen source as discussed below.

The process of the invention can be carried out such that the fluoropolymer resin is dried under static conditions or dynamic conditions. "Static conditions" means that the fluoropolymer is not subjected to agitation such as by stirring or shaking during drying although drying in equipment such as tray drying in an oven result in circulation of the drying gas by convection. "Dynamic conditions" means that the process is carried while moving the fluoropolymer resin such as by stirring or shaking or actively passing a drying gas through the fluoropolymer resin which

may additionally cause movement the fluoropolymer resin. Heat transfer and mass transfer can be facilitated by the use of dynamic conditions, for example, flowing the drying gas through the polymer bed. Preferably, the process of the invention is carried out under dynamic conditions.

- 5 Preferred equipment and process conditions for drying under dynamic conditions is disclosed by Egres, Jr. et al. US 5,391,709, in which the wet fluoropolymer resin is deposited as a shallow bed on fabric and dried by passing heated air through the bed, preferably from top to bottom.

As used in this application, "oxygen source" means any chemical  
10 source of available oxygen. "Available oxygen" means oxygen capable of reacting as an oxidizing agent. Preferably, the oxygen source is air, oxygen rich gas, or ozone-containing gas. "Oxygen rich gas" means pure oxygen and gas mixtures containing greater than about 21% oxygen by volume, preferably oxygen enriched air. Preferably, oxygen rich gas  
15 contains at least about 22% oxygen by volume. "Ozone containing gas" means pure ozone and gas mixtures containing ozone, preferably ozone enriched air. Preferably, the content of ozone in the gas mixture is at least about 10 ppm ozone by volume.

One preferred oxygen source for practice of the present invention is  
20 ozone containing gas, preferably ozone enriched air. Ozone enriched air as the drying gas can be provided by employing an ozone generator which feeds ozone into the drying air as it is supplied to the drying apparatus used. Another preferred oxygen source is oxygen rich gas, preferably oxygen enriched air. Oxygen enriched air as the drying gas can be  
25 provided by feeding oxygen into the drying air as it is supplied to the drying apparatus used. Oxygen enriched air can also be provided by semipermeable polymeric membrane separation systems.

Temperatures of drying gas during drying can be in the range of about 100°C to about 300°C. Higher temperature drying gases shorten  
30 the drying time and facilitate the reduction of thermally induced discoloration. However, temperatures of the drying gas should not cause the temperature of the fluoropolymer resin to reach or exceed its melting point which will cause the fluoropolymer to fuse. For melt-processible fluoropolymers, preferred drying gas temperatures are 160°C to about

10°C below the melting point of the fluoropolymer. The end use properties of PTFE resin can be adversely affected by temperatures well below its melting point. Preferably, PTFE resin is dried using drying gas at a temperature of about 100°C to about 200°C, more preferably, about  
5 150°C to about 180°C.

The time necessary to carry out the process of the invention will vary with factors including the thickness of the wet fluoropolymer resin being dried, the temperature employed, the oxygen source employed and the rate of circulation of the drying gas. When ozone containing gas is  
10 used as the oxygen source, the reduction of thermally induced discoloration can be accomplished during normal drying times, preferably in the range of about 15 minutes to 10 hours. If desired, the process of the invention can be continued after the fluoropolymer resin is dry for the purposes of reducing thermally induced discoloration.

15 In a preferred form of the invention, the exposing of the wet fluoropolymer resin to an oxygen source during drying is carried out in the presence of alkali metal salt. In this form of the invention, it is preferred for the oxygen source to be ozone containing gas.

Any of variety of alkali metal salts can be used. The anion in the  
20 alkali metal salt preferably is non-reactive with components of the dispersion although hydroxide can be beneficial since higher pH values can promote reduction of discoloration. Preferred alkali metal salts are sodium salts, lithium salts and potassium salts with potassium salts being most preferred. Examples of suitable alkali metal salts are KCl, K<sub>2</sub>CO<sub>3</sub>,  
25 K<sub>2</sub>SO<sub>4</sub>, NaOH, NaCl, LiOH and LiCl.

The presence of alkali metal salt during drying is preferably provided by adding alkali metal salt to the aqueous medium prior to separating the wet fluoropolymer resin from said aqueous medium. For example, the alkali metal salt can be added before coagulation or after  
30 coagulation but before the aqueous medium is removed. Preferably, the alkali metal salt is added prior to coagulation.

When added to the aqueous medium, the amount of alkali metal salt can vary depending upon the type of salt added, the severity of the discoloration and other conditions employed in the process. Preferably,

the amount of alkali metal salt added to the dispersion prior to coagulation is about 5 ppm to about 50,000 ppm based on the weight of dry fluoropolymer, more preferably about 50 ppm to about 25,000 ppm, and most preferably about 150 ppm to about 10,000 ppm.

5           In a preferred form of the invention, the process further comprises pretreating the aqueous fluoropolymer dispersion, preferably by exposing the aqueous fluoropolymer dispersion to an oxidizing agent. In the practice of the present invention employing a pretreatment, the pretreatment may or may not result in reduction of thermally induced  
10   discoloration as measured by % change in  $L^*$  if employed alone without subsequently exposing the wet fluoropolymer resin to an oxygen source during drying. Moreover, it is possible that the thermally induced discoloration of the fluoropolymer resin may be increased, i.e., the discoloration worsens, by the pretreatment alone without subsequently  
15   exposing the wet fluoropolymer resin to an oxygen source during drying. However, the additive effect of the pretreatment in combination with exposing the wet fluoropolymer resin to an oxygen source during drying in accordance with the invention preferably provides an improvement over the reduction of thermally induced discoloration provided only by exposing  
20   the wet fluoropolymer resin to an oxygen source during drying. The reduction of thermally induced discoloration measured by % change in  $L^*$  on the CIELAB color scale provided by pretreating in combination with exposing the wet fluoropolymer resin to an oxygen source during drying is preferably at least about 10% greater than the % change in  $L^*$  on the  
25   CIELAB color scale provided by only exposing the wet fluoropolymer resin to an oxygen source under the same conditions during drying, more preferably 20% greater, still more preferably 30% greater, most preferably 50% greater.

          Pretreatment of the aqueous fluoropolymer dispersion can be  
30   accomplished by a variety of techniques. One preferred pretreatment comprises exposing the aqueous fluoropolymer dispersion to ultraviolet light in the presence of an oxygen source. For the practice of this pretreatment, the aqueous fluoropolymer dispersion is preferably first diluted with water to a concentration less than the concentration of the as

polymerized aqueous fluoropolymer dispersion because, depending upon the equipment used, exposure of ultraviolet light can be more effective for reducing discoloration for dilute dispersions. Preferred concentrations are about 2 weight percent to about 30 weight percent, more preferably about 5 2 weight percent to about 20 weight percent.

Ultraviolet light has a wavelength range of about 10 nm to about 400 nm and has been described to have bands including: UVA (315 nm to 400 nm), UVB (280 nm to 315 nm), and UVC (100 nm to 280 nm). Preferably, the ultraviolet light employed has a wavelength in the UVC 10 band.

Any of various types of ultraviolet lamps can be used as the source of ultraviolet light. For example, submersible UV clarifier/sterilizer units sold for the purposes of controlling algae and bacterial growth in ponds are commercially available and may be used for the practice of this 15 pretreatment. These units include a low-pressure mercury-vapor UVC lamp within a housing for the circulation of water. The lamp is protected by a quartz tube so that water can be circulated within the housing for exposure to ultraviolet light. Submersible UV clarifier/sterilizer units of this type are sold, for example, under the brand name Pondmaster by Danner 20 Manufacturing, Inc. of Islandia NY. For continuous treatment processes, the dispersion can be circulated through units of this type to expose the dispersion to ultraviolet light. Single pass or multiple pass treatments can be employed.

Dispersion can also be processed in a batch operation in a 25 container suitable for exposure to ultraviolet light in the presence of an oxygen source. In this pretreatment, it is desirable for a suitably protected ultraviolet lamp to be immersed in the dispersion. For example, a vessel normally used for coagulation of the aqueous fluoropolymer dispersion to produce fluoropolymer resin can be used for carrying out the process of 30 this pretreatment by immersing the ultraviolet lamp in the dispersion held in this vessel. The dispersion can be circulated or stirred if desired to facilitate exposure to the ultraviolet light. When the oxygen source is a gas as discussed below, circulation may be achieved or enhanced by injecting the oxygen source into the dispersion. Ultraviolet lamps with

protective quartz tubes of the type employed in the submersible UV clarifier/sterilizer units can be employed for immersion in dispersion after being removed from their housing. Other ultraviolet lamps such as medium-pressure mercury-vapor lamps can also be used with the lamp suitably protected for immersion in the dispersion such as by enclosing the lamp in a quartz photowell. A borosilicate glass photowell can also be used although it may decrease effectiveness by filtering ultraviolet light in the UVC and UVB bands. Suitable medium-pressure mercury vapor lamps are sold by Hanovia of Fairfield, New Jersey.

10 As used for this pretreatment, "oxygen source" means any chemical source of available oxygen. "Available oxygen" means oxygen capable of reacting as an oxidizing agent. The oxygen source employed in accordance with this pretreatment is preferably selected from the group consisting of air, oxygen rich gas, ozone containing gas and hydrogen peroxide. "Oxygen rich gas" means pure oxygen and gas mixtures containing greater than about 21% oxygen by volume, preferably oxygen enriched air. Preferably, oxygen rich gas contains at least about 22% oxygen by volume. "Ozone containing gas" means pure ozone and gas mixtures containing ozone, preferably ozone enriched air. Preferably, the content of ozone in the gas mixture is at least about 10 ppm ozone by volume.

For the practice of this pretreatment, one preferred oxygen source is an ozone containing gas. Another preferred oxygen source for the practice of this pretreatment is hydrogen peroxide. For providing the presence of the oxygen source in the dispersion during exposure to ultraviolet light, air, oxygen rich gas or ozone containing gas can be injected continuously or intermittently into the dispersion, preferably in stoichiometric excess, to provide the oxygen source during the exposure to ultraviolet light. Hydrogen peroxide can be added to the dispersion, also preferably in stoichiometric excess, by adding hydrogen peroxide solution. The concentration of hydrogen peroxide is preferably about 0.1 weight % to about 10 weight % based on fluoropolymer solids in the dispersion.

Ultraviolet light with an oxygen source is effective at ambient or moderate temperatures and thus elevated temperatures are typically not required for the practice of this pretreatment. In a preferred form of this pretreatment, exposing the aqueous fluoropolymer dispersion to ultraviolet  
5 light in the presence of an oxygen source is carried out at a temperature of about 5°C to about 70°C, preferably about 15°C to about 70°C.

The time for carrying out this pretreatment with vary with factors including the power of the ultraviolet light used, the type of oxygen source, processing conditions, etc. Preferred times for this pretreatment are about  
10 15 minutes to about 10 hours.

Another preferred pretreatment comprises exposing the aqueous fluoropolymer dispersion to light having a wavelength of 10 nm to 760 nm in the presence of an oxygen source and photocatalyst. For the practice of this pretreatment, the aqueous fluoropolymer dispersion is preferably  
15 first diluted with water to a concentration less than the concentration of the as polymerized aqueous fluoropolymer dispersion because, depending upon the equipment used, exposure to light can be more effective for reducing discoloration for dilute dispersions. Preferred concentrations are about 2 weight percent to about 30 weight %, more preferably about 2  
20 weight percent to about 20 weight percent.

Light to be employed in accordance with this pretreatment has a wavelength range or about 10 nm to about 760 nm. This wavelength range includes ultraviolet light having a wavelength range of about 10 nm to about 400 nm. Ultraviolet light has a wavelength range or about 10 nm  
25 to about 400 nm and has been described to have bands including: UVA (315 nm to 400 nm), UVB (280 nm to 315 nm), and UVC (100 nm to 280 nm). Light to be employed in accordance with this pretreatment also includes visible light having a wavelength range of about 400 nm to about 760 nm.

30 Any of various types of lamps can be used as the source of light. For example, submersible UV clarifier/sterilizer units sold for the purposes of controlling algae and bacterial growth in ponds are commercially available and may be used for the practice of this pretreatment. These units include a low-pressure mercury-vapor UVC lamp within a housing for

the circulation of water. The lamp is protected by a quartz tube so that water can be circulated within the housing for exposure to ultraviolet light. Submersible UV clarifier/sterilizer units of this type are sold, for example, under the brand name Pondmaster by Danner Manufacturing, Inc. of Islandia NY. For continuous treatment processes, the dispersion can be circulated through units of this type to expose the dispersion to light. Single pass or multiple pass treatments can be employed.

Dispersion can also be processed in a batch operation in a container suitable for exposure to light in the presence of an oxygen source and photocatalyst. In this pretreatment, it is desirable for a suitably protected lamp to be immersed in the dispersion. For example, a vessel normally used for coagulation of the aqueous fluoropolymer dispersion to produce fluoropolymer resin can be used for carrying out the process of this pretreatment by immersing the lamp in the dispersion held in this vessel. The dispersion can be circulated or stirred if desired to facilitate exposure to the light. When the oxygen source is a gas as discussed below, circulation may be achieved or enhanced by injecting the oxygen source into the dispersion. Ultraviolet lamps with protective quartz tubes of the type employed in the submersible UV clarifier/sterilizer units can be employed for immersion in dispersion after being removed from their housing. Other ultraviolet lamps such as medium-pressure mercury vapor lamps can also be used with the lamp suitably protected for immersion in the dispersion such as by enclosing the lamp in a quartz photowell. A borosilicate glass photowell can also be used although it may decrease effectiveness by filtering ultraviolet light in the UVC and UVB bands. Suitable medium-pressure mercury vapor lamps are sold by Hanovia of Fairfield, New Jersey.

As used in this pretreatment, "oxygen source" means any chemical source of available oxygen. "Available oxygen" means oxygen capable of reacting as an oxidizing agent. The oxygen source employed in accordance with the present this pretreatment is preferably selected from the group consisting of air, oxygen rich gas, ozone containing gas and hydrogen peroxide. "Oxygen rich gas" means pure oxygen and gas mixtures containing greater than about 21% oxygen by volume, preferably



oxygen enriched air. Preferably, oxygen rich gas contains at least about 22% oxygen by volume. "Ozone containing gas" means pure ozone and gas mixtures containing ozone, preferably ozone enriched air. Preferably, the content of ozone in the gas mixture is at least about 10 ppm ozone by volume.

For the practice of this pretreatment, one preferred oxygen source is an ozone containing gas. Another preferred oxygen source for the practice of this pretreatment is hydrogen peroxide. For providing the presence of the oxygen source in the dispersion during exposure to ultraviolet light, air, oxygen rich gas or ozone containing gas can be injected continuously or intermittently into the dispersion, preferably in stoichiometric excess, to provide the oxygen source during the exposure to light. Hydrogen peroxide can be added to the dispersion, also preferably in stoichiometric excess, by adding hydrogen peroxide solution.

The concentration of hydrogen peroxide is preferably about 0.1 weight % to about 10 weight % based on fluoropolymer solids in the dispersion.

Any of a variety of photocatalysts may be used in the practice of this pretreatment. Preferably, the photocatalyst is a heterogeneous photocatalyst. Most preferably, the heterogeneous photocatalyst is selected from form the group consisting of titanium dioxide and zinc oxide. For example, titanium dioxide sold under the tradename Degussa P25 having a primary particle size of 21 nm and being a mixture of 70% anatase and 30% rutile titanium dioxide has been found to be an effective heterogeneous photocatalyst. Heterogeneous photocatalyst can be used by dispersing it into the dispersion prior to exposure to light. Preferred levels of heterogenous photocatalyst are about 1 ppm to about 100 ppm based on fluoropolymer solids in the dispersion.

Light with an oxygen source and photocatalyst is effective at ambient or moderate temperatures and thus elevated temperatures are typically not required for the practice of this pretreatment. In a preferred process in accordance with this pretreatment, exposing the aqueous fluoropolymer dispersion to ultraviolet light in the presence of an oxygen source is carried out at a temperature of about 5°C to about 70°C, preferably about 15°C to about 70°C.

The time for carrying out this pretreatment will vary with factors including the power of the ultraviolet light used, the type of oxygen source, processing conditions, etc. Preferred times for this pretreatment are about 15 minutes to about 10 hours.

- 5 Another preferred pretreatment comprises exposing the aqueous fluoropolymer dispersion to hydrogen peroxide. For the practice of this pretreatment, the aqueous fluoropolymer dispersion is preferably first diluted with water to a concentration less than the concentration of the as polymerized aqueous fluoropolymer dispersion. Preferred concentrations  
10 are about 2 weight percent to about 30 weight percent, more preferably about 2 weight percent to about 20 weight percent.

- Exposing of the aqueous fluoropolymer dispersion to hydrogen peroxide is preferably carried out by adding hydrogen peroxide to said aqueous fluoropolymer dispersion, preferably in an amount of about 0.1  
15 weight % to about 10 weight percent based on weight of fluoropolymer solids. Preferably, the exposing of the aqueous fluoropolymer dispersion to hydrogen peroxide is carried out at a temperature of about 10°C to about 70 °C, preferably about 25°C to about 60°C. The time employed for the exposure of the aqueous fluoropolymer dispersion is preferably  
20 about 1 hour to about 48 hours.

- It is preferable for the practice of this pretreatment to also inject air, oxygen rich gas, or ozone containing gas into said fluoropolymer dispersion during the exposing of the aqueous fluoropolymer dispersion to the hydrogen peroxide. "Oxygen rich gas" means pure oxygen and gas  
25 mixtures containing greater than about 21% oxygen by volume, preferably oxygen enriched air. Preferably, oxygen rich gas contains at least about 22% oxygen by volume. "Ozone containing gas" means pure ozone and gas mixtures containing ozone, preferably ozone enriched air. Preferably, the content of ozone in the gas mixture is at least about 10 ppm ozone by  
30 volume. Introduction of such gases can be accomplished by injecting the gases into the aqueous fluoropolymer dispersion.

Preferably, the exposing of the aqueous fluoropolymer dispersion to hydrogen peroxide is carried out in the presence of  $\text{Fe}^{+2}$ ,  $\text{Cu}^{+1}$ , or  $\text{Mn}^{+2}$

ions. Preferably, the amount of  $\text{Fe}^{+2}$ ,  $\text{Cu}^{+1}$ , or  $\text{Mn}^{+2}$  ions is about 0.1 ppm to about 100 ppm based on fluoropolymer solids in the dispersion.

Although the process can also be carried out in a continuous process, batch processes are preferable since batch processes facilitate controlled times for exposure of the hydrogen peroxide with the aqueous fluoropolymer dispersion to achieve the desired reduction in thermally induced discoloration. A batch process can be carried out in any suitable tank or vessel of appropriate materials of construction and, if desired, has heating capability to heat the dispersion during treatment. For example, a batch process can be carried out in a vessel normally used for coagulation of the aqueous fluoropolymer dispersion which typically includes an impeller which can be used to stirring the dispersion during treatment. Injection of air, oxygen rich gas, or ozone containing gas can also be employed to impart agitation to the dispersion.

Another preferred pretreatment comprises exposing the aqueous fluoropolymer dispersion to oxidizing agent selected from the group consisting of hypochlorite salts and nitrite salts. For the practice of this pretreatment, the aqueous fluoropolymer dispersion is preferably first diluted with water to a concentration less than the concentration of the as polymerized aqueous fluoropolymer dispersion. Preferred concentrations are about 2 weight percent to about 30 weight percent, more preferably about 2 weight percent to about 20 weight percent.

Exposing of the aqueous fluoropolymer dispersion to oxidizing agent selected from the group consisting of hypochlorite salts and nitrite salts is preferably carried out by adding the oxidizing agent to the aqueous fluoropolymer dispersion, preferably in an amount of about 0.05 weight % to about 5 weight percent based on weight of fluoropolymer solids. Preferred hypochlorite salts for addition to the dispersion are sodium hypochlorite or potassium hypochlorite. Sodium hypochlorite or potassium hypochlorite are preferably used in an amount of about 0.05 weight % to about 5 weight percent based on weight of fluoropolymer solids. Provided that aqueous medium of the dispersion is sufficiently alkaline such as by containing sodium hydroxide, hypochlorite can also be generated in situ by injecting chlorine gas into the dispersion. Preferred nitrite salts for addition

to the dispersion are sodium nitrite, potassium nitrite and ammonium nitrite. Sodium nitrite, potassium nitrite and ammonium nitrite are preferably used in an amount of about 0.5 weight % to about 5 weight percent based on weight of fluoropolymer solids.

- 5            Preferably, the exposing of the aqueous fluoropolymer dispersion to the oxidizing agent is carried out at a temperature of about 10°C to about 70°C. The exposure time with the aqueous fluoropolymer dispersion is preferably about 5 minutes to about 3 hours.

- 10           It is preferable for the practice of this pretreatment to also introduce air, oxygen rich gas, or ozone containing gas into said fluoropolymer dispersion during the exposing of the aqueous fluoropolymer dispersion to the oxidizing agent. "Oxygen rich gas" means pure oxygen and gas mixtures containing greater than about 21% oxygen by volume, preferably oxygen enriched air. Preferably, oxygen rich gas contains at least about  
15           22% oxygen by volume. "Ozone containing gas" means pure ozone and gas mixtures containing ozone, preferably ozone enriched air. Preferably, the content of ozone in the gas mixture is at least about 10 ppm ozone by volume. Introduction of such gases can be accomplished by injecting such gases into the aqueous fluoropolymer dispersion.

- 20           Although the pretreatment can also be carried out in a continuous process, batch processes are preferable since batch processes facilitate controlled times for exposure of the hypochlorite salt or nitrite salt with the aqueous fluoropolymer dispersion to achieve the desired reduction in thermally induced discoloration. A batch process can be carried out in any  
25           suitable tank or vessel of appropriate materials of construction and, if desired, has heating capability to heat the dispersion during treatment. For example, a batch process can be carried out in a vessel normally used for coagulation of the aqueous fluoropolymer dispersion which typically includes an impeller which can be used to stirring the dispersion during  
30           treatment. Injection of air, oxygen rich gas, or ozone containing gas can also be employed to impart agitation to the dispersion.

Another preferred pretreatment comprises adjusting the pH of the aqueous medium of the aqueous fluoropolymer dispersion to greater than about 8.5 and exposing the aqueous fluoropolymer dispersion to an

oxygen source. For the practice of this pretreatment, the aqueous fluoropolymer dispersion is preferably first diluted with water to a concentration less than the concentration of the as polymerized aqueous fluoropolymer dispersion. Preferred concentrations are about 2 weight percent to about 30 weight percent, more preferably about 2 weight percent to about 20 weight percent.

The pH of the aqueous fluoropolymer dispersion preferably is adjusted to about 8.5 to about 11. More preferably, the pH of the aqueous medium of the aqueous fluoropolymer dispersion is adjusted to about 9.5 to about 10.

The pH can be adjusted for the practice of this pretreatment by addition of a base which is sufficiently strong to adjust the pH of the aqueous fluoropolymer dispersion to the desired level and which is otherwise compatible with the processing of the dispersion and the end use properties of the fluoropolymer resin produced. Preferred bases are alkali metal hydroxides such as sodium hydroxide or potassium hydroxide. Ammonium hydroxide can also be used.

As used for this pretreatment, "oxygen source" means any chemical source of available oxygen. "Available oxygen" means oxygen capable of reacting as an oxidizing agent. The oxygen source employed in accordance with this pretreatment is preferably selected from the group consisting of air, oxygen rich gas, ozone containing gas and hydrogen peroxide. "Oxygen rich gas" means pure oxygen and gas mixtures containing greater than about 21% oxygen by volume, preferably oxygen enriched air. Preferably, oxygen rich gas contains at least about 22% oxygen by volume. "Ozone containing gas" means pure ozone and gas mixtures containing ozone, preferably ozone enriched air. Preferably, the content of ozone in the gas mixture is at least about 10 ppm ozone by volume.

For the practice of this pretreatment, one preferred oxygen source is an ozone containing gas. Another preferred oxygen source is for the practice of this pretreatment is hydrogen peroxide. For providing the exposure of dispersion to the oxygen source, air, oxygen rich gas or ozone containing gas can be injected continuously or intermittently into the

dispersion, preferably in stoichiometric excess. Hydrogen peroxide can be added to the dispersion, also preferably in stoichiometric excess, by adding hydrogen peroxide solution. The concentration of hydrogen peroxide is preferably about 0.1 weight % to about 10 weight % based on fluoropolymer solids in the dispersion.

Preferably, the exposing of the aqueous fluoropolymer dispersion to oxygen source is carried out at a temperature of about 10°C to about 95°C, more preferably about 20°C to about 80°C, most preferably about 25°C to about 70°C. The time employed for the exposure of the aqueous fluoropolymer dispersion to oxygen source is preferably about 5 minutes to about 24 hours.

Although the process can also be carried out in a continuous process, batch processes are preferable since batch processes facilitate controlled times for exposure of the hydrogen peroxide with the aqueous fluoropolymer dispersion to achieve the desired reduction in thermally induced discoloration. A batch process can be carried out in any suitable tank or vessel of appropriate materials of construction and, if desired, has heating capability to heat the dispersion during treatment. For example, a batch process can be carried out in a vessel normally used for coagulation of the aqueous fluoropolymer dispersion which typically includes an impeller which can be used to stirring the dispersion during treatment. Injection of air, oxygen rich gas, or ozone containing gas can also be employed to impart agitation to the dispersion.

More than one pretreatment can be used if desired.

The process of the present invention is useful for fluoropolymer resin which exhibits thermally induced discoloration which may range from mild to severe. The process is especially useful for aqueous fluoropolymer dispersion which contains hydrocarbon surfactant which causes the thermally induced discoloration, preferably aqueous fluoropolymer dispersion that is polymerized in the presence of hydrocarbon surfactant.

The process of the invention is especially useful when the fluoropolymer resin prior to treatment exhibits significant thermally induced discoloration compared to equivalent commercial fluoropolymers. The

invention is advantageously employed when the fluoropolymer resin has an initial thermally induced discoloration value ( $L^*_i$ ) at least about 4 L units below the  $L^*$  value of equivalent fluoropolymer resin of commercial quality manufactured using ammonium perfluorooctanoate fluorosurfactant. The invention is more advantageously employed when the  $L^*_i$  value is at least about 5 units below the  $L^*$  value of such equivalent fluoropolymer resin, even more advantageously employed when the  $L^*_i$  value is at least 8 units below the  $L^*$  value of such equivalent fluoropolymer resin, still more advantageously employed when the  $L^*_i$  value is at least 12 units below the  $L^*$  value of such equivalent fluoropolymer resin, and most advantageously employed when the  $L^*_i$  value is at least 20 units below the  $L^*$  value of such equivalent fluoropolymer resin.

After the fluoropolymer resin is treated in accordance with the process of the invention, the resulting fluoropolymer resin is suitable for end use applications appropriate for the particular type of fluoropolymer resin. Fluoropolymer resin produced by employing the present invention exhibits reduced thermally induced discoloration without detrimental effects on end use properties.

20

### **TEST METHODS**

Raw Dispersion Particle Size (RDPS) of polymer particles is measured using a Zetasizer Nano-S series dynamic light scattering system manufactured by Malvern Instruments of Malvern, Worcestershire, United Kingdom. Samples for analysis are diluted to levels recommended by the manufacturer in 10x10x45 mm polystyrene disposable cuvettes using deionized water that has been rendered substantially free of particles by passing it through a sub-micron filter. The sample is placed in the Zetasizer for determination of  $Dv(50)$ .  $Dv(50)$  is the median particle size based on volumetric particle size distribution, i.e. the particle size below which 50% of the volume of the population resides.

30

The melting point ( $T_m$ ) of melt-processible fluoropolymers is measured by Differential Scanning Calorimeter (DSC) according to the procedure of ASTM D 4591-07 with the melting temperature reported

being the peak temperature of the endotherm of the second melting. For PTFE homopolymer, the melting point is also determined by DSC. The unmelted PTFE homopolymer is first heated from room temperature to 380°C at a heating rate of 10°C and the melting temperature reported is the peak temperature of the endotherm on first melting.

Comonomer content is measured using a Fourier Transform Infrared (FTIR) spectrometer according to the method disclosed in U.S. Patent No. 4,743,658, col. 5, lines 9-23 with the following modifications. The film is quenched in a hydraulic press maintained at ambient conditions. The comonomer content is calculated from the ratio of the appropriate peak to the fluoropolymer thickness band at 2428 cm<sup>-1</sup> calibrated using a minimum of three other films from resins analyzed by fluorine-19 NMR to establish true comonomer content. For instance, the %HFP content is determined from the absorbance of the HFP band at 982 cm<sup>-1</sup>, and the PEVE content is determined by the absorbance of the PEVE peak at 1090 cm<sup>-1</sup>.

Melt flow rate (MFR) of the melt-processible fluoropolymers are measured according to ASTM D 1238-10, modified as follows: The cylinder, orifice and piston tip are made of a corrosion-resistant alloy, Haynes Stellite 19, made by Haynes Stellite Co. The 5.0 g sample is charged to the 9.53 mm (0.375 inch) inside diameter cylinder, which is maintained at 372°C±1°C, such as disclosed in ASTM D 2116-07 for FEP and ASTM D 3307-10 for PFA. Five minutes after the sample is charged to the cylinder, it is extruded through a 2.10 mm (0.0825 inch) diameter, 8.00 mm (0.315 inch) long square-edge orifice under a load (piston plus weight) of 5000 grams. Other fluoropolymers are measured according to ASTM D 1238-10 at the conditions which are standard for the specific polymer.

#### Measurement of Thermally Induced Discoloration

##### 30 1) Color Determination

The L\* value of fluoropolymer resin samples is determined using the CIELAB color scale, details of which are published in CIE Publication 15.2 (1986). CIE L\*a\*b\* (CIELAB) is the color space specified by the International Commission on Illumination (French Commission



internationale de l'éclairage). It describes all the colors visible to the human eye. The three coordinates of CIELAB represent the lightness of the color ( $L^*$ ), its position between red/magenta and green ( $a^*$ ), and its position between yellow and blue ( $b^*$ ).

5    **2) PTFE Sample Preparation and Measurement**

The following procedure is used to characterize the thermally induced discoloration of PTFE polymers including modified PTFE polymers. 4.0 gram chips of compressed PTFE powder are formed using a Carver stainless steel pellet mold (part # 2090-0) and a Carver manual  
10    hydraulic press (model 4350), both manufactured by Carver, Inc. of Wabash, Indiana. In the bottom of the mold assembly is placed a 29mm diameter disk of 0.1mm thick Mylar film. 4 grams of dried PTFE powder are spread uniformly within the mold opening poured into the mold and distributed evenly. A second 29mm disk is placed on top of the PTFE and  
15    the top plunger is placed in the assembly. The mold assembly is placed in the press and pressure is gradually applied until 8.27 MPa (1200 psi) is attained. The pressure is held for 30 seconds and then released. The chip mold is removed from the press and the chip is removed from the mold. Mylar films are peeled from the chip before subsequent sintering.  
20    Typically for each polymer sample, two chips are molded.

An electric furnace is heated is heated to 385°C. Chips to be sintered are placed in 4 inch x 5 inch (10.2 cm x 12.7 cm) rectangular aluminum trays which are 2 inches (5.1 cm) in depth. The trays are placed in the furnace for 10 minutes after which they are removed to  
25    ambient temperature for cooling.

4 gm chips processed as described above are evaluated for color using a HunterLab ColorQuest XE made by Hunter Associates Laboratory, Inc. of Reston, Virginia. The ColorQuest XE sensor is standardized with the following settings, Mode: RSIN, Area View: Large and Port Size: 2.54  
30    cm. The instrument is used to determine the  $L^*$  value of fluoropolymer resin samples using the CIELAB color scale.

For testing, the instrument is configured to use CIELAB scale with D65 Illuminant and 10° Observer. The  $L^*$  value reported by this

colorimeter is used to represent developed color with  $L^*$  of 100 indicating a perfect reflecting diffuser (white) and  $L^*$  of 0 representing black.

An equivalent fluoropolymer resin of commercial quality manufactured using ammonium perfluorooctanoate fluorosurfactant is used as the standard for color measurements. For the Examples in this application illustrating the invention for PTFE fluoropolymer, an equivalent commercial quality PTFE product made using ammonium perfluorooctanoate fluorosurfactant as the dispersion polymerization surfactant is TEFLON® 601A. Using the above measurement process, the resulting color measurement for TEFLON® 601A is  $L^*_{\text{Std-PTFE}} = 87.3$

### **3) Melt-Processible Fluoropolymers Sample Preparation and Measurement**

The following procedure is used to characterize discoloration of melt-processible fluoropolymers, such as FEP and PFA, upon heating. A 10.16 cm (4.00 inch) by 10.16 cm (4.00 inch) opening is cut in the middle of a 20.32 cm (8.00 inch) by 20.32 cm (8.00 inch) by 0.254 mm (0.010 inch) thick metal sheet to form a chase. The chase is placed on a 20.32 cm (8.00 inch) by 20.32 cm (8.00 inch) by 1.59 mm (1/16 inch) thick molding plate and covered with Kapton® film that is slightly larger than the chase. The polymer sample is prepared by reducing size, if necessary, to no larger than 1 mm thick and drying. 6.00 grams of polymer sample is spread uniformly within the mold opening. A second piece of Kapton® film that is slightly larger than the chase is placed on top of the sample and a second molding plate, which has the same dimensions as the first, is placed on top of the Kapton® film to form a mold assembly. The mold assembly is placed in a P-H-I 20 ton hot press model number SP-210C-X4A-21 manufactured by Pasadena Hydraulics Incorporated of El Monte, California that is set at 350°C. The hot press is closed so the plates are just contacting the mold assembly and held for 5 minutes. The pressure on the hot press is then increased to 34.5 MPa (5,000 psi) and held for an additional 1 minute. The pressure on the hot press is then increased from 34.5 MPa (5,000 psi) to 137.9 MPa (20,000 psi) over the time span of 10 seconds and held for an additional 50 seconds after reaching 137.9 MPa (20,000 psi). The mold assembly is removed from the hot press, placed

between the blocks of a P-H-I 20 ton hot press model number P-210H manufactured by Pasadena Hydraulics Incorporated that is maintained at ambient temperature, the pressure is increased to 137.9 MPa (20,000 psi), and the mold assembly is left in place for 5 minutes to cool. The mold assembly is then removed from the ambient temperature press, and the sample film is removed from the mold assembly. Bubble-free areas of the sample film are selected and 2.86 cm (1-1/8 inch) circles are stamped out using a 1-1/8 inch arch punch manufactured by C. S. Osborne and Company of Harrison, New Jersey. Six of the film circles, each of which has a nominal thickness of 0.254 mm (0.010 inch) and nominal weight of 0.37 gram are assembled on top of each other to create a stack with a combined weight of 2.2 +/- 0.1 gram.

The film stack is placed in a HunterLab ColorFlex spectrophotometer made by Hunter Associates Laboratory, Inc. of Reston, Virginia, and the  $L^*$  is measured using a 2.54 cm (1.00 inch) aperture and the CIELAB scale with D65 Illuminant and 10° Observer.

An equivalent fluoropolymer resin of commercial quality manufactured using ammonium perfluorooctanoate fluorosurfactant is used as the standard for color measurements. For the Examples in this application illustrating the invention for FEP fluoropolymer resin, an equivalent commercial quality FEP resin made using ammonium perfluorooctanoate fluorosurfactant as the dispersion polymerization surfactant is DuPont TEFLON® 6100 FEP. Using the above measurement process, the resulting color measurement for DuPont TEFLON® 6100 FEP is  $L^*_{\text{Std-FEP}} = 79.7$ .

4) % change in  $L^*$  with respect to the standard is used to characterize the change in thermally induced discoloration of the fluoropolymer resin after treatment as defined by the following equation

$$\% \text{ change in } L^* = (L^*_t - L^*_i) / (L^*_{\text{Std}} - L^*_i) \times 100$$

$L^*_i$  = Initial thermally induced discoloration value, the measured value for  $L$  on the CIELAB scale for fluoropolymer resins prior to treatment to reduce

thermally induced discoloration measured using the disclosed test method for the type of fluoropolymer.

$L^*_t$  = Treated thermally induced discoloration value, the measured value

- 5 for L on the CIELAB scale for fluoropolymer resins after treatment to reduce thermally induced discoloration measured using the disclosed test method for the type of fluoropolymer.

Standard for PTFE: measured  $L^*_{Std-PTFE} = 87.3$

- 10 Standard for FEP: measured  $L^*_{Std-FEP} = 79.7$

### **EXAMPLES**

#### Apparatus for Drying of PTFE Polymer

- 15 A laboratory dryer for simulating commercially dried PTFE Fine Powder is constructed as follows: A length of 4 inch (10.16 cm) stainless steel pipe is threaded on one end and affixed with a standard stainless steel pipe cap. In the center of the pipe cap is drilled a 1.75 inch (4.45 cm) hole through which heat and air source is introduced. A standard 4 inch
- 20 (10.16 cm) pipe coupling is sawed in half along the radial axis and the sawed end of one piece is butt welded to the end of the pipe, opposite the pipe cap. Overall length of this assembly is approximately 30 inches (76.2 cm) and the assembly is mounted in the vertical position with the pipe cap at the top. For addition of a control thermocouple, the 4 inch pipe
- 25 assembly is drilled and tapped for a 1/4 inch (6.35 mm) pipe fitting at a position 1.75 inch (4.45 cm) above the bottom of the assembly. A 1/4 inch (6.35 mm) male pipe thread to 1/8 inch (3.175 mm) Swagelok fitting is threaded into the assembly and drilled through to allow the tip of a 1/8 inch (3.175 mm) J-type thermocouple to be extended through the fitting and
- 30 held in place at the pipe's radial center. For addition of a other gases, the 4 inch (10.16 cm) pipe assembly is drilled and tapped for a 1/4 inch (6.35 mm) pipe fitting at a position 180° from the thermocouple port and higher at 3.75 inch (9.5 cm) above the bottom of the assembly. A 1/4 inch (6.35

mm) male pipe thread to 1/4 inch (6.35 mm) Swagelok fitting is threaded into the assembly and drilled through to allow the open end of a 1/4 inch (6.35 mm) stainless steel tube to be extended through the fitting and held in place at the pipe's radial center. The entire pipe assembly is wrapped  
5 with heat resistant insulation that can easily withstand 200°C continuous duty.

The dryer bed assembly for supporting polymer is constructed as follows: A 4 inch (10.16 cm) stainless steel pipe nipple is sawed in half along the radial axis and onto the sawed end of one piece is tack welded  
10 stainless steel screen with 1.3 mm wire size and 2.1 mm square opening. Filter media of polyether ether ketone (PEEK) or Nylon 6,6 fabric is cut into a 4 inch (10.16 cm) disk and placed on the screen base. A 4 inch (10.16 cm) disk of stainless steel screen is placed on top of the filter fabric to hold it securely in place. Fabrics used include a Nylon 6,6 fabric and  
15 PEEK fabric having the characteristics described in US Patent 5,391,709. In operation, approximately 1/4 inch (6.35 mm) of polymer is placed uniformly across the filter bed and the dryer bed assembly is screwed into the bottom of the pipe assembly.

The heat and air source for this drying apparatus is a Master heat  
20 gun, model HG-751B, manufactured by Master Appliance Corp. of Racine, WI. The end of this heat gun can be snugly introduced through and supported by the hole in the cap at the top of the pipe assembly. Control of air flow is managed by adjusting a damper on the air intake of the heat gun. Control of temperature is maintained by an ECS Model 800-377  
25 controller, manufactured by Electronic Control Systems, Inc of Fairmont WV. Adaptation of the controller to the heat gun is made as follows: The double pole power switch of the heat gun is removed. All power to the heat gun is routed through the ECS controller. The blower power is supplied directly from the ECS controller on/off switch. The heater circuit  
30 is connected directly to the ECS controller output. The thermocouple on the pipe assembly which is positioned above the polymer bed serves as the controller measurement device.

The apparatus described above is typically used to dry PTFE Fine Powder at 170°C and can easily maintain that temperature to within  $\pm 1^\circ\text{C}$ .

### Apparatus for Drying of FEP Polymer

Equipment similar in design to that described in Apparatus for Drying of PTFE Polymer is used except the scale is increased so the dryer bed assembly is 8 inch (20.32 cm) in diameter and the stainless steel screen is a USA standard testing sieve number 20 mesh. Unless otherwise noted, the apparatus is used to dry FEP for two hours with 180°C air and can easily maintain that temperature to within  $\pm 1^\circ\text{C}$ . Typical polymer loading is 18 grams dry weight of polymer.

- 5
- 10 A secondary dryer bed assembly is produced by the addition of three evenly spaced nozzles with a centerline 3.0 cm above the polymer bed. The nozzles can be used to introduce additional gasses to the drying air. One of many possible configurations is to connect an AQUA-6 portable ozone generator manufactured by A2Z Ozone of Louisville,
- 15 Kentucky to each of the nozzles.

### 10 watt UVC Light Source

- For experiments using 10 watt UVC light sources, the 254nm lamps are obtained from 10 watt Pondmaster® submersible UV clarifier/sterilizer units manufactured by Danner Manufacturing, Inc. of Islandia, NY. These units, commonly used in the aquaculture industry, consist of 4 major components: (1) A ballast which provides the proper power supply. (2) A low pressure mercury vapor lamp which emits UVC radiation upon activation. (3) A quartz tube which protects the lamp and electronics from water damage while allowing short wavelength UV light to pass. (4) A dark plastic outer housing which is threaded at one end so as to screw onto the ballast and provide a seal around the quartz tube, thereby protecting lamp and electronics from water penetration. The housing is also designed to allow water to flow from one end of the protected lamp to the other end while preventing hazardous UV light from escaping the housing. For purposes of this experimentation, the plastic housing is removed and the threaded end is removed by saw. The treaded adapter is then screwed back into the ballast, thereby sealing the quartz tube to
- 20
- 25
- 30

the ballast but eliminating the black plastic UV shield. In this way the light source is made useful for batch (ie. non flow through) experiments.

Light intensity is measured with a meter that has the capability of reading up to 20.0 milliwatts/cm<sup>2</sup> (mW/cm<sup>2</sup>) by positioning three sensors (245nm UVC, 310nm UVB and 365nm UVA) four inches from the quartz protective tube. Measurements: UVC is 1.06 mW/cm<sup>2</sup>, UVB is 33.7 microwatt/cm<sup>2</sup> and UVA is 19.2 microwatt/cm<sup>2</sup>.

#### 450 watt Hanovia Lamp Light Source

For experiments using a 450 watt Hanovia lamp, a Model PC451.050 450 watt medium pressure mercury vapor lamp, manufactured by Hanovia, Inc. of Fairfield, New Jersey is used with the following setup: An Ace Glass Incorporated, Model 6386-20, 2000 ml jacketed filter reactor body is fitted with an Ace Glass, Inc. Model 5846-60 bottom PTFE plug in which a recess is machined to support a 48 mm diameter, jacketed immersion photowell. The photowell is connected to a circulating cooling bath of sufficient capacity to keep the coolant temperature exiting the photowell below 40°C. The lamp is operated with an appropriately matched power supply such as the Ace Glass Model No. 7830-58. A quartz photowell (Ace Glass Part # 7874-23) or a borosilicate photowell (Ace Glass Part # 7875-30) may be used although it may decrease effectiveness by filtering some ultraviolet light in the UVC and UVB bands.

Light intensity is measured with a meter (UVP Model UVX Radiometer) that has the capability of reading up to 20.0 milliwatts/cm<sup>2</sup> (mW/cm<sup>2</sup>) by positioning three sensors (245nm UVC (UVP Model UVX-25), 310nm UVB (UVP Model UVX-31) and 365nm UVA (UVP Model UVX36)) 3.5 inches from the borosilicate well. When the Hanovia 450watt lamp is fully heated up, the UVC reads 10.11 mW/cm<sup>2</sup>, the UVB reads 9.37 mW/cm<sup>2</sup> and the UVA reads 17.0 mW/cm<sup>2</sup>.

When similar measurement is made with the quartz photowell, even before the Hanovia 450watt lamp is fully heated up, the light intensity is so strong as to reach the maximum measurement capability of the light meter used.

## Fluoropolymer Preparation

### PTFE - Preparation of Hydrocarbon Stabilized PTFE Dispersion

To a 12 liter, horizontally disposed, jacketed, stainless steel autoclave with a two blade agitator is added 5200 gm of deionized, deaerated water. To the autoclave is added an additional 500 gm of deionized, deaerated water which contains 0.12 gm of Pluronic® 31R1. The autoclave is sealed and placed under vacuum. The autoclave pressure is raised to 30 psig (308 kPa) with nitrogen and vented to atmospheric pressure. The autoclave is pressured with nitrogen and vented 2 more times. Autoclave agitator speed is set at 65 RPM. 20 ml of initiator solution containing 1.0 gm of ammonium persulfate (APS) per liter of deionized, deaerated water is added to the autoclave.

The autoclave is heated to 90°C and TFE is charged to the autoclave to bring the autoclave pressure to 400 psig (2.86 MPa). 150 ml of an initiator solution composed of 11.67 gm of 70% active disuccinic acid peroxide (DSP), 0.167 gm of APS and 488.3 gm of deionized water is charged to the autoclave at 80 ml/min. After the autoclave pressure drops 10 psi (69 kPa) from the maximum pressure observed during injection of initiator solution, the autoclave pressure is brought back to 400 psig (2.86 MPa) with TFE and maintained at that pressure for the duration of the polymerization. After 100 gm of TFE has been fed since kickoff, an aqueous surfactant solution containing 5733 ppm of SDS hydrocarbon stabilizing surfactant and 216 ppm of iron sulfate heptahydrate is pumped to the autoclave at a rate of 4 ml/min until 185 ml of surfactant solution has been added. After approximately 70 minutes since kickoff, 1500 gm of TFE has been added to the autoclave. The agitator is stopped, the autoclave is vented to atmospheric pressure and the dispersion is cooled and discharged. Solids content of the dispersion is 18-19 wt%. Dv(50) raw dispersion particle size (RDPS) is 208 nm.

### Isolation of PTFE Dispersion

To a clean glass resin kettle having internal dimensions 17 cm deep and 13 cm in diameter is charged 600 gm of 5 wt % dispersion. The dispersion is agitated with a variable speed, IKA Works, Inc., RW20 digital



- overhead stirrer affixed with a 6.9 cm diameter, rounded edge three blade impeller having a 45° downward pumping pitch. The following sequence is executed until the dispersion has completely coagulated as indicated by the separation of white PTFE polymer from a clear aqueous phase: At
- 5 time zero, agitation speed is set at 265 revolutions per minute (RPM) and 20 ml of a 20 wt % aqueous solution of ammonium carbonate is slowly added to the resin kettle. At 1 minute from time zero, the agitator speed is raised to 565 RPM and maintained until the dispersion is completely coagulated. Once coagulated, the clear aqueous phase is removed by
- 10 suction and 600 ml of cold (approximately 6°C), deionized water is added. The slurry is agitated at 240 RPM for 5 minutes until agitation is halted and the wash water removed from the resin kettle. This washing procedure is repeated two more times with the final wash water being separated from the polymer by vacuum filtration as indicated below.
- 15 A ceramic filtration funnel (10 cm internal diameter) is placed on a vacuum flask with rubber sealing surface. A 30 cm by 30 cm lint free nylon filter cloth is placed in the filtration funnel and the washed polymer and water is poured into the funnel. A vacuum is pulled on the vacuum flask and once the wash water is removed, 1200 ml of additional deionized
- 20 water is poured over the polymer and pulled through the polymer into the vacuum flask. Polymer thus coagulated, washed and isolated is removed from the filter cloth for further processing.

#### FEP: Preparation of Hydrocarbon Stabilized TFE/HFP/PEVE Dispersion

- 25 A cylindrical, horizontal, water-jacketed, paddle-stirred, stainless steel reactor having a length to diameter ratio of about 1.5 and a water capacity of 10 gallons (37.9 L) is charged with 60 pounds (27.2 kg) of deionized water. The reactor temperature then is increased to 103 °C while agitating at 46 rpm. The agitator speed is reduced to 20 rpm and the
- 30 reactor is vented for 60 seconds. The reactor pressure is increased to 15 psig (205 kPa) with nitrogen. The agitator speed is increased to 46 rpm while cooling to 80°C. The agitator speed is reduced to 20 rpm and a vacuum is pulled to 12.7 psia (88 kPa). A solution containing 500 ml of deaerated deionized water, 0.5 grams of Pluronic® 31R1 solution and 0.3

g of sodium sulfite is drawn into the reactor. With the reactor paddle agitated at 20 rpm, the reactor is heated to 80 °C, evacuated and purged three times with TFE. The agitator speed is increased to 46 rpm and the reactor temperature then is increased to 103 °C. After the temperature has become steady at 103 °C, HFP is added slowly to the reactor until the pressure is 430 psig (3.07 MPa). 112 ml of liquid PEVE is injected into the reactor. Then TFE is added to the reactor to achieve a final pressure of 630 psig (4.45 MPa). Then 80 ml of freshly prepared aqueous initiator solution containing 2.20 wt% of ammonium persulfate (APS) is charged into the reactor. Then, this same initiator solution is pumped into the reactor at a TFE to initiator solution mass ratio of twenty-to-one for the remainder of the polymerization after polymerization has begun as indicated by a 10 psi (69 kPa) drop in reactor pressure, i.e. kickoff. Additional TFE is also added to the reactor beginning at kickoff at a rate of 0.06 lb/min (0.03 kg/min) subject to limitation in order to prevent the reactor from exceeding the maximum desired limit of 650 psig (4.58 MPa) until a total of 12.0 lb (5.44 kg) of TFE has been added to the reactor after kickoff. Furthermore, liquid PEVE is added to the reactor beginning at kickoff at a rate of 0.3 ml/min for the duration of the reaction.

After 4.0 lb (1.8 kg) of TFE has been fed since kickoff, an aqueous surfactant solution containing 45,176 ppm of SDS hydrocarbon stabilizing surfactant and 60,834 ppm of 30% ammonium hydroxide solution is pumped to the autoclave at a rate of 0.2 ml/min. The aqueous surfactant solution pumping rate is increased to 0.3 ml/min after 6.0 lb (2.7 kg) of TFE has been fed since kickoff, then to 0.4 ml/min after 8.0 lb (3.6 kg) of TFE has been fed since kickoff, to 0.6 ml/min after 10.0 lb (4.5 kg) of TFE has been fed since kickoff, and finally to 0.8 ml/min after 11.0 lb (5.0 kg) of TFE has been fed since kickoff resulting in a total of 47 ml of surfactant solution added during reaction. The total reaction time is 201 minutes after initiation of polymerization during which 12.0 lb (5.44 kg) of TFE and 60 ml of PEVE are added. At the end of the reaction period, the TFE feed, PEVE feed, the initiator feed and surfactant solution feed are stopped; an additional 25 ml of surfactant solution is added to the reactor, and the reactor is cooled while maintaining agitation. When the temperature of the

reactor contents reaches 90°C, the reactor is slowly vented. After venting to nearly atmospheric pressure, the reactor is purged with nitrogen to remove residual monomer. Upon further cooling, the dispersion is discharged from the reactor at below 70 °C.

- 5            Solids content of the dispersion is 20.07 wt% and Dv(50) raw dispersion particle size (RDPS) is 143.2 nm. 703 grams of wet coagulum is recovered on cleaning the autoclave. The TFE/HFP/PEVE terpolymer (FEP) has a melt flow rate (MFR) of 29.6 gm/10 min, an HFP content of 9.83 wt%, a PEVE content of 1.18 wt%, and a melting point of 256.1 °C.

10

#### Isolation of FEP Dispersion

The dispersion is coagulated by freezing the dispersion at -30 °C for 16 hours. The dispersion is thawed and the water is separated from the solids by filtering through a 150 micron mesh filter bag model

- 15    NMO150P1SHS manufactured by The Strainrite Companies of Auburn, Maine.

#### Thermally Induced Discoloration

- 20            Dried polymer is characterized as described above in the Test Methods - Measurement of Thermally Induced Discoloration as applicable to the type of polymer used in the following Examples.

#### Comparative Example 1: PTFE with Hydrocarbon Stabilizing Surfactant - No Treatment

- 25            A quantity of PTFE dispersion as described above is diluted to 5 wt % solids with deionized water. The dispersion is coagulated and isolated via the method described above (Isolation of PTFE Dispersion). Polymer thus obtained is then dried at 170°C for 1 hour using the PTFE drier described above in Apparatus for Drying of PTFE Polymer. Dried polymer is characterized for thermally induced discoloration as described in the
- 30    Test Methods Measurement of Thermally Induced Discoloration for PTFE. Resulting value for  $L^*_i$  is 43.9, indicating extreme discoloration of the polymer upon thermal processing for untreated polymer. The measured color is shown in Table 1.

Example 1a: PTFE PTFE, Dried with Ozone at 1/2 Power

A quantity of PTFE Dispersion as described above is diluted to 5 wt% solids with deionized water. The dispersion is coagulated and isolated via the method described above (Coagulation and Isolation of PTFE Dispersion). Polymer thus obtained is then dried at 170°C for 1 hour using the PTFE drier described above (Apparatus for Drying of PTFE Polymer). During the hour of drying, 100 cc/min of ozone enriched air is introduced into the dryer. Ozone is produced by passing 100 cc/min of air into a Clearwater Technologies, Inc. Model CD-10 ozone generator which is operated at 1/2 power setting. Dried polymer is characterized as described in the Test Methods Measurement of Thermally Induced Discoloration for PTFE. L\* obtained for this polymer is 63.7 with a % change in L\* of 45.6% indicating a much improved color after treatment. The measured color is shown in Table 1.

Example 1b: PTFE, Dried with Ozone at Full Power

Example 1 is repeated except the ozone generator is operated at full power. L\* obtained for this polymer is 65.9 with a % change in L\* of 50.7% indicating a much improved color after treatment. The measured color is shown in Table 1.

Comparative Example 2 - PTFE, UVC, 1wt% H<sub>2</sub>O<sub>2</sub> on polymer, O<sub>2</sub> Injection, 3 Hours, 60°C

To a glass beaker is added 155gm of PTFE dispersion as prepared above having 19.4% solids and 1.0 gm of 30 wt% hydrogen peroxide. The net weight is raised to 600 gm with deionized water, thus reducing the %solids to 5 wt%. A total of 1800 gms of dispersion thus prepared is added to a 2000 ml jacketed resin kettle. The dispersion is heated to 60°C with agitation aided by continuous injection with 100 cc/min of oxygen through two sintered glass, fine bubble, sparge tubes. Two 10 watt 254nm UV lights are immersed in the dispersion. The lights are energized for 3 hours. 1200 gm of the treated dispersion is coagulated and isolated as described above. Half of the resulting wet polymer is dried in the apparatus for drying of PTFE polymers at 170 °C for 1 hour using only air as the drying gas. Dried polymer is characterized as described in the Test

Methods Measurement of Thermally Induced Discoloration for PTFE. L\* obtained for this polymer is 75.9 with a % change in L\* of 73.7%. The measured color is shown in Table 1.

Example 2 - PTFE, UVC, 1wt% H<sub>2</sub>O<sub>2</sub> on polymer, O<sub>2</sub> Injection, 3 Hours, 60°C

The remaining half of wet polymer obtained from Comparative Example 2 after coagulation and isolation is dried in the apparatus for drying of PTFE polymers described above with the addition of ozone enriched air. During the hour of drying at 170 °C, 100 cc/min of ozone enriched air is introduced into the dryer. Ozone is produced by passing 100 cc/min of air into a Clearwater Technologies, Inc. Model CD-10 ozone generator which is operated at the full power setting. Dried polymer is characterized for Thermally Induced Discoloration. L\* obtained for this polymer is 84.9 with a % change in L\* of 94.5% indicating a much improved color after treatment. The measured color is shown in Table 1.

Comparative Example 3 - PTFE, 0.33-0.5 wt% NaOCl on poly, 1 Hour, Ambient Temp

To a glass resin kettle is added 155gm of PTFE dispersion as described above having 19.4% solids. The net weight is raised to 600 gm with deionized water, thus reducing the %solids to 5 wt%. To the dispersion is added 1.0 gm of 10-15 wt% sodium hypochlorite solution. The dispersion is agitated at 240 rpm for 1 hour with a variable speed, IKA Works, Inc., RW20 digital overhead stirrer affixed with a 6.9 cm diameter, rounded edge three blade impeller having a 45° downward pumping pitch. The resulting, treated dispersion is coagulated and isolated as described above, dried in the apparatus for drying of PTFE polymers using only ambient air as the drying gas and finally characterized for Thermally Induced Discoloration. L\* obtained for this polymer is 57.2 with a % change in L\* of 30.6%. The measured color is shown in Table 1.

Example 3 - PTFE, 0.33-0.5 wt% NaOCl on poly, 1 Hour, Ambient Temp

The procedure of Comparative Example 3 is repeated and after coagulation and isolation, the wet polymer is dried in the apparatus for drying of PTFE polymers with the addition of ozone enriched air. During  
5 the hour of drying at 170 °C, 100 cc/min of ozone enriched air is introduced into the dryer. Ozone is produced by passing 100 cc/min of air into a Clearwater Technologies, Inc. Model CD-10 ozone generator which is operated at the full power setting. Dried polymer is characterized for Thermally Induced Discoloration. L\* obtained for this polymer is 84.9 with  
10 a % change in L\* of 94.5% indicating a much improved color after treatment. The measured color is shown in Table 1.

Comparative Example 4 - PTFE, NaOH pH=9.9, Oxygen, 3.0 Hours @50°C

15 To a 2000 ml jacketed resin kettle is added 465 gm of PTFE Dispersion as described above having a solids content of 19.4 wt%. Net weight is raised to 1800 gm with deionized water. While agitating at 300 rpm, the dispersion is heated to 50°C by setting the appropriate temperature on the jacket circulating bath. Once at temperature, pH of the  
20 dispersion is adjusted to 9.9 by adding approximately 8 drops of 50 wt% sodium hydroxide solution to the resin kettle. The dispersion is sparged with oxygen through a 25 mm diameter sintered glass, fine bubble, sparge tube. Dispersion temperature is held constant and agitation is continued for 3.0 hours. 1200 gm of the treated dispersion is coagulated and  
25 isolated as described above. Half of the resulting wet polymer is dried at 170 °C for one hour in the apparatus for drying of PTFE polymers using only air as the drying gas. Dried Polymer is characterized for Thermally Induced Discoloration. L\* obtained for this polymer is 54.2 with a % change in L\* of 23.7%. The measured color is shown in Table 1.

30

Example 4 - PTFE, NaOH pH=9.9, Oxygen, 3.0 Hours @50°C

The remaining half of wet polymer obtained from Comparative Example 4 after coagulation and isolation is dried at 170 °C for 1 hour in

the apparatus for drying of PTFE polymers with the addition of ozone enriched air. During the hour of drying, 100 cc/min of ozone enriched air is introduced into the dryer. Ozone is produced by passing 100 cc/min of air into a Clearwater Technologies, Inc. Model CD-10 ozone generator  
5 which is operated at the full power setting. The dried polymer is characterized for Thermally Induced Discoloration.  $L^*$  obtained for this polymer is 81.3 with a % change in  $L^*$  of 86.2% indicating a much improved color after treatment. The measured color is shown in Table 1.

10 Comparative Example 5 (PTFE, NaOH pH=9.9, Oxygen, 1.0 Hour @50°C

To a 2000 ml jacketed resin kettle is added 310 gm of PTFE Dispersion as described above having a solids content of 19.4 wt%. Net weight is raised to 1200 gm with deionized water. While agitating at 300 rpm, the dispersion is heated to 50°C by setting the appropriate  
15 temperature on the jacket circulating bath. Once at temperature, pH of the dispersion is adjusted to 9.9 by adding approximately 5 drops of 50 wt% sodium hydroxide solution to the resin kettle. The dispersion is sparged with oxygen through a 25 mm diameter sintered glass, fine bubble, sparge tube. Dispersion temperature is held constant and agitation is continued  
20 for 1.0 hour. The treated dispersion is coagulated and isolated as described above. Half of the resulting wet polymer is dried in the apparatus for drying of PTFE polymers at 170 °C for one hour using only air as the drying gas. Dried polymer is characterized for Thermally Induced Discoloration.  $L^*$  obtained for this polymer is 49.3 with a %  
25 change in  $L^*$  of 12.4%. The measured color is shown in Table 1.

Example 5 - PTFE, NaOH pH=9.9, Oxygen, 1.0 Hours @50°C

The remaining half of wet polymer obtained from Comparative Example 5 after coagulation and isolation is dried in the apparatus for drying of PTFE polymers at 170 °C for one hour with the addition of ozone  
30 enriched air. During the hour of drying, 100 cc/min of ozone enriched air is introduced into the dryer. Ozone is produced by passing 100 cc/min of air into a Clearwater Technologies, Inc. Model CD-10 ozone generator which is operated at the full power setting. Dried polymer is characterized

for Thermally Induced Discoloration. L\* obtained for this polymer is 75.5 with a % change in L\* of 72.8% indicating a much improved color after treatment. The measured color is shown in Table 1.

5

Table 1

Examples	L* drying with air	% change in L*	L* drying with ozone enriched air	% change in L with ozone enriched air
Comp Ex 1 (No Treatment)	43.9			
Example 1a	-	-	63.7	45.6%
Example 1b	-	-	65.9	50.7%
Comp Ex 2	75.9	73.7%	-	-
Example 2	-	-	84.9	94.5%
Comp Ex 3	57.2	30.6%	-	-
Example 3	-	-	84.9	94.5%
Comp Ex 4	54.2	23.7%	-	-
Example 4	-	-	81.3	86.2%
Comp Ex 5	49.3	12.4%	-	-
Example 5	-	-	75.5	72.8%

#### Comparative Example 6 - FEP – No Treatment

Aqueous FEP dispersion polymerized as described above is diluted to 5 weight percent solids with deionized water. The dispersion is coagulated by freezing the dispersion at -30 °C for 16 hours. The dispersion is thawed and the water is separated from the solids by filtering through a 150 micron mesh filter bag model NMO150P1SHS manufactured by The Strainrite Companies of Auburn, Maine. The solids are divided to allow the sample to be dried by more the one technique.



A first portion of polymer is dried for 2 hours with 180°C air in the equipment described under Apparatus for Drying of FEP Polymer solids using only air as the drying gas. The dried powder is molded to produce color films to characterize for thermally induced discoloration as described in the Test Methods section above as Measurement of Thermally Induced Discoloration for FEP. L\* obtained for this polymer is 44.8. The measured color is shown in Table 2.

#### Example 7 - FEP – Ozone Drying

Another portion of polymer prepared in Comparative Example 6 is dried for 2 hours with 180°C air that is enriched with ozone in the equipment described under Apparatus for Drying of FEP Polymer with the dryer bed assembly with three evenly spaced nozzles. Each nozzle is connected to an AQUA-6 portable ozone generator manufactured by A2Z Ozone of Louisville, Kentucky, which is operated during the drying process. L\* obtained for this polymer is 55.8 with a % change in L\* of 31.5% indicating a much improved color after treatment. The measured color is shown in Table 2.

#### Example 8 - FEP - Pretreatment with UVC + Ozone Injection

Aqueous FEP dispersion polymerized as described Comparative Example 6 is diluted to 5 weight percent solids with deionized water and preheated to 40 °C in a water bath. A fresh FeSO<sub>4</sub> solution is prepared by diluting 0.0150 g of FeSO<sub>4</sub>·7H<sub>2</sub>O to 100 ml using deaerated deionized water. 1200 ml of the FEP dispersion, 4 ml of the FeSO<sub>4</sub> solution, and 2 ml of 30 wt % H<sub>2</sub>O<sub>2</sub> are added to a 2000 ml jacketed glass reactor with internal diameter of 10.4 cm, which has 40 °C water circulating through the reactor jacket, and the contents are mixed. Two sparge tubes that each have a 12 mm diameter by 24 mm long, fine-bubble, fritted-glass cylinder produced by LabGlass as part number 8680-130 are placed in the reactor, and each is connected to an AQUA-6 portable ozone generator described above. The ozone generators are turned on and used to bubble 1.18 standard L/min (2.5 standard ft<sup>3</sup>/hr) of ozone enriched air through the

dispersion. The dispersion is allowed to equilibrate for 5 minutes. A 10 watt UVC light as described in 10 watt UVC Light Source is placed in the reactor. The UVC lamp is turned on to illuminate the dispersion while injection with ozone enriched air and controlling temperature at 40 °C.

- 5 After three hours, the lamp is extinguished and the ozone enriched air is stopped. The dispersion is coagulated, filtered, dried and molded as described in Comparative Example 6 to compare the differences between drying with air only and ozone enriched air. L\* obtained for polymer dried with air only is 58.4 with a % change in L\* of 39.0%. L\* obtained for  
10 polymer dried with ozone enriched air is 76.2 with a % change in L\* of 90.0% indicating a much improved color after treatment. The measured color is shown in Table 2.

#### Example 9 – FEP - Pretreatment with UVC + Oxygen Injection

- 15 Treatment is conducted utilizing the same conditions as Example 8 except 1.0 standard L/min of oxygen is bubbled through a sparge tube with a 25 mm diameter fine fritted glass disc sparge tube produced by Ace Glass as part number 7196-20 in place of ozone. Dried polymer is characterized for Thermally induced Discoloration.

- 20 L\* obtained for polymer dried with air only is 55.2 with a % change in L\* of 29.8%. L\* obtained for polymer dried with ozone enriched air is 60.4 with a % change in L\* of 44.7% indicating a much improved color after treatment. The measured color is shown in Table 2.

#### Example 10– FEP -Pretreatment with H<sub>2</sub>O<sub>2</sub> Treatment

- Aqueous FEP dispersion polymerized as described in Comparative Example 6 is diluted to 5 weight percent solids with deionized water. 1200 ml of the FEP dispersion preheated to 50 °C in a water bath. The preheated dispersion and 2 ml of 30 wt % H<sub>2</sub>O<sub>2</sub> are added to a 2000 ml  
30 jacketed glass reactor with internal diameter of 13.3 cm (5-1/4 inches) that has 50 °C water circulating through the reactor jacket. An impeller with four 3.18 cm (1.25 inch) long flat blades set at a 45° angle and two sparge tubes that each have a 12 mm diameter by 24 mm long fine-bubble,

fritted-glass cylinder produced by LabGlass as part number 8680-130 are placed in the reactor. The sparge tubes are connected to an air supply that is passed through a Drierite gas purification column model 27068 produced by W.A. Hammond Drierite Company of Xenia, Ohio, and the air supply is adjusted to deliver 1.42 standard L/min (3.0 standard ft<sup>3</sup>/hr). The  
5 agitator is set at 60 rpm. After 5 minutes of mixing, the dispersion temperature is 49.5 °C and the reaction timer is started. After 45 minutes of reaction, 50 ml of deionized water and 2 ml of 30 wt % H<sub>2</sub>O<sub>2</sub> are added to offset evaporative losses. The reaction is ended after 16 hours by  
10 stopping the agitator, ceasing the air flow, discontinuing the hot water circulation, and then removing the dispersion from the reactor. The dispersion is coagulated, filtered, dried and molded as described in Comparative Example 6 to compare the differences between drying with air only and ozone enriched air. L\* obtained for polymer dried with air only  
15 is 35.2 with a % change in L\* of -27.5%. L\* obtained for polymer dried with ozone enriched air is 63.7 with a % change in L\* of 54.2% indicating a much improved color after treatment. The measured color is shown in Table 2. It is to be noted that the pretreatment in this example results in dried polymer in air alone showing a severe decrease in the value of L\* as  
20 compared to untreated polymer. However, drying the pretreated polymer in ozone enriched air results in a greater % change in L\* than polymer dried in ozone enriched air with no pretreatment (see Comparative Example 6 which shows a % change of L\* = 31.5%). This shows that the pretreatment of dispersion with H<sub>2</sub>O<sub>2</sub> confers an added beneficial effect in  
25 improving the thermally induced discoloration when drying polymer with ozone enriched air.

#### Example 11 – FEP - Pretreatment with UVC + Catalyst + Oxygen Injection

Aqueous FEP dispersion polymerized as described Comparative  
30 Example 6 is diluted to 5 weight percent solids with deionized water and preheated to 40 °C in a water bath. A TiO<sub>2</sub> solution is produced by sonicating 0.0030 g of Degussa P-25 TiO<sub>2</sub> lot Kontrollnummer 1263 diluted to 6 ml with deionized water. 1200 ml of the FEP dispersion, all 6 ml of

the  $\text{TiO}_2$  solution, and 2 ml of 30 wt %  $\text{H}_2\text{O}_2$  are added to a 2000 ml jacketed glass reactor with internal diameter of 10.4 cm, which has 40 °C water circulating through the reactor jacket, and the contents are mixed. A sparge tube with a 25 mm diameter fine-bubble, fritted-glass disc sparge

5 tube produced by Ace Glass as part number 7196-20 is placed in the reactor, and 1.0 standard L/min of oxygen is bubbled through the dispersion. The dispersion is allowed to equilibrate for 5 minutes. A 10 watt UVC light as described in 10 watt UVC Light Source is placed in the reactor. The UVC lamp is turned on to illuminate the dispersion while

10 injection with oxygen and controlling temperature at 40 °C. After three hours, the lamp is extinguished and the sparge gas is stopped. The dispersion is coagulated, filtered, dried and molded as described in Comparative Example 6 to compare the differences between drying with air only and ozone enriched air.  $L^*$  obtained for polymer dried with air only

15 is 63.3 with a % change in  $L^*$  of 53.0%.  $L^*$  obtained for polymer dried with ozone enriched air is 79.0 with a % change in  $L^*$  of 98.0% indicating a much improved color after treatment. The measured color is shown in Table 2.

Table 2

Examples	L* drying with air	% change in L	L* drying with ozone enriched air	% change in L with ozone enriched air
Comp Ex 6  (No Treatment)	44.8	-	-	-
Example 7	-	-	55.8	31.5%
Example 8	58.4	39.0%	76.2	90.0%
Example 9	55.2	29.8%	60.4	44.7%
Example 10	35.2	-27.5%	63.7	54.2%
Example 11	63.3	53.0%	79.0	98.0%

#### Comparative Example 7 – PTFE – No Treatment

- An aqueous PTFE dispersion is made similar to the method
- 5 described above (PTFE - Preparation of Hydrocarbon Stabilized PTFE Dispersion) but with addition to the reactor of 4100 grams of SDS per million grams of dry polymer. The resulting dispersion is diluted to 15 wt% solids with deionized water and is isolated as described above (Isolation of PTFE Dispersion) with the exception that the 600 grams of dispersion is
- 10 15 wt% solids rather than the 5 wt% solids described above.
- Approximately 55 gm of the wet polymer is then dried at 180°C for 1 hour using the PTFE drier described above (Apparatus for Drying of PTFE Polymer). Dried polymer is characterized for thermally induced discoloration as described in the Test Methods Measurement of Thermally
- 15 Induced Discoloration for PTFE. The measured L\* value is 34.0 and is shown in Table 3.

Example 12 – PTFE – Drying with Ozone Enriched Air

Approximately 55 gm of the wet polymer as produced in Comparative Example 7 – PTFE is dried at 180°C for 1 hour using the PTFE drier described above (Apparatus for Drying of PTFE Polymer) with the addition of ozone enriched air. Ozone is produced by passing 300 cc/min of air into a ClearWater Tech. LLC Model CD-10 ozone generator which is operated at the full power setting. Dried polymer is characterized for thermally induced discoloration as described in the Test Methods Measurement of Thermally Induced Discoloration for PTFE. The measured L\* value and the % change in L\* as calculated relative to Comparative Example 7 – PTFE are shown in Table 3.

Example 12 - PTFE demonstrates the benefit of employing ozone enriched air as the oxygen source.

Table 3 – Effect of Ozone as Oxygen Source

Example	O3-Air cc/min	L*	% Chg in L*
Comp. Ex. 7 – PTFE	0	34.0	
Example 12 – PTFE	300	47.9	26.1

Example 13 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, KCl

An aqueous PTFE dispersion is made similar to the method described above (PTFE - Preparation of Hydrocarbon Stabilized PTFE Dispersion) but with addition to the reactor of 4100 grams of SDS per million grams of dry polymer. The resulting dispersion is diluted to 15 wt% solids with deionized water. 0.145 gm of the alkali metal salt, KCl, is added to 600 gm of the dilute dispersion and thoroughly mixed. The resulting mixture is isolated as described above (Isolation of PTFE Dispersion) with the exception that the 600 grams of dispersion is 15 wt% solids rather than the 5 wt% solids described above. Approximately 55 gm of the wet polymer is then dried at 180°C for 1 hour using the PTFE drier described above (Apparatus for Drying of PTFE Polymer) with the addition of ozone enriched air. Ozone is produced by passing 300 cc/min of air

into a Clearwater Technologies, Inc. Model CD-10 ozone generator which is operated at the full power setting. Dried polymer is characterized for thermally induced discoloration as described in the Test Methods Measurement of Thermally Induced Discoloration for PTFE. The measured L\* value and the % change in L\* as calculated relative to Example 12 – PTFE are shown in Table 4.

Examples 14, 15 and 16 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, KCl

The procedure of Example 13 – PTFE is repeated except that the amount of alkali metal salt, KCl, is increased to 0.515 gm, 0.687 gm and 0.762 gm, respectively. The measured L\* value and the % change in L\* as calculated relative to Example 12 – PTFE are shown in Table 4.

The examples of Table 4 demonstrate the significant improvements in L\* with the presence of alkali metal salt during the exposure of the wet fluoropolymer resin to an oxygen source during drying.

Table 4 – Oxygen Source and Effect of Alkali Metal Salt				
Example	O3-Air cc/min	KCl, gm	L*	% Chg in L*
Example 12 – PTFE	300	0	47.9	
Example 13 – PTFE	300	0.145	66.7	47.7
Example 14 – PTFE	300	0.515	67.7	50.3
Example 15 – PTFE	300	0.687	78.6	77.9
Example 16 – PTFE	300	0.762	80.5	82.7

Example 17 – PTFE – Drying with Ozone Enriched Air

An aqueous PTFE dispersion is made as described above (PTFE - Preparation of Hydrocarbon Stabilized PTFE Dispersion). The resulting dispersion is diluted to 15 wt% solids with deionized water and is isolated as described above (Isolation of PTFE Dispersion) with the exception that the 600 grams of dispersion is 15 wt% solids rather than the 5 wt% solids described above. Approximately 55 gm of the wet polymer is then dried at 170°C for 1 hour using the PTFE drier described above (Apparatus for

Drying of PTFE Polymer) with the addition of ozone enriched air. Ozone is produced by passing 100 cc/min of air into a ClearWater Tech, LLC Model CD-10 ozone generator which is operated at the full power setting. Dried polymer is characterized for thermally induced discoloration as described in the Test Methods Measurement of Thermally Induced Discoloration for PTFE. The measured L\* value is 55.3 and is shown in Table 5.

Example 18 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, NaOH

An aqueous PTFE dispersion is made as described above (PTFE - Preparation of Hydrocarbon Stabilized PTFE Dispersion). A quantity of dispersion is diluted to 15 wt% solids with deionized water. 0.135 gm of the alkali metal salt, NaOH, is added to 600 gm of the dilute dispersion and thoroughly mixed. The resulting mixture is isolated as described above (Isolation of PTFE Dispersion) with the exception that the 600 grams of dispersion is 15 wt% solids rather than the 5 wt% solids described above. Approximately 55 gm of the wet polymer is then dried at 170°C for 1 hour using the PTFE drier described above (Apparatus for Drying of PTFE Polymer) with the addition of ozone enriched air. Ozone is produced by passing 100 cc/min of air into a Clearwater Technologies, Inc. Model CD-10 ozone generator which is operated at the full power setting. Dried polymer is characterized for thermally induced discoloration as described in the Test Methods Measurement of Thermally Induced Discoloration for PTFE. The measured L\* value and the % change in L\* as calculated relative to Example 17 – PTFE are shown in Table 5.

Example 19 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, NaCl

The procedure of Example 18 – PTFE is repeated except that 0.114 gm of NaCl is substituted for the NaOH. The measured L\* value and the % change in L\* as calculated relative to Example 17 – PTFE are shown in Table 5.



Example 20 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, NaCl

The procedure of Example 18 – PTFE is repeated except that 0.195 gm of NaCl is substituted for the NaOH. The measured L\* value and the % change in L\* as calculated relative to Example 17 – PTFE are shown in Table 5.

Example 21 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, LiCl

The procedure of Example 18 – PTFE is repeated except that 0.083 gm of LiCl is substituted for the NaOH. The measured L\* value and the % change in L\* as calculated relative to Example 17 – PTFE are shown in Table 5.

Example 22 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, LiCl

The procedure of Example 18 – PTFE is repeated except that 0.468 gm of LiCl is substituted for the NaOH. The measured L\* value and the % change in L\* as calculated relative to Example 17 – PTFE are shown in Table 5.

Example 23 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, K<sub>2</sub>CO<sub>3</sub>

The procedure of Example 18 – PTFE is repeated except that 0.150 gm of K<sub>2</sub>CO<sub>3</sub>·1.5H<sub>2</sub>O is substituted for the NaOH. The measured L\* value and the % change in L\* as calculated relative to Example 17 – PTFE are shown in Table 5.

Example 24 – PTFE – Drying with Ozone Enriched Air in the Presence of Alkali Metal Salt, K<sub>2</sub>SO<sub>4</sub>

The procedure of Example 18 – PTFE is repeated except that 0.171 gm of K<sub>2</sub>SO<sub>4</sub> is substituted for the NaOH. The measured L\* value and the % change in L\* as calculated relative to Example 17 – PTFE are shown in Table 5.

Table 5 – Effect of Alkali Metal Salts				
Example	Salt	Salt, gm	L*	% Chg in L*
Example 17 – PTFE		0	55.3	
Example 18 – PTFE	NaOH	0.135	83.2	87.2
Example 19 – PTFE	NaCl	0.114	80.6	79.1
Example 20 – PTFE	NaCl	0.195	83.5	88.1
Example 21 – PTFE	LiCl	0.083	64.2	27.8
Example 22 – PTFE	LiCl	0.468	80.2	80.9
Example 23 – PTFE	K <sub>2</sub> CO <sub>3</sub> ·1.5H <sub>2</sub> O	0.150	72.7	52.4
Example 24 – PTFE	K <sub>2</sub> SO <sub>4</sub>	0.171	73.0	53.4

**What is claimed is:**

1. Process for reducing thermally induced discoloration of fluoropolymer resin, said fluoropolymer resin produced by polymerizing fluoromonomer in an aqueous dispersion medium to form aqueous  
5 fluoropolymer dispersion and isolating said fluoropolymer from said aqueous medium by separating wet fluoropolymer resin from the aqueous medium and drying to produce said fluoropolymer resin, said process comprising:  
    exposing said wet fluoropolymer resin to an oxygen source during  
10 drying.
2. The process of claim 1 wherein said process reduces thermally induced discoloration by at least about 10% as measured by % change in L\* on the CIELAB color scale.
3. The process of any of the preceding claims wherein said  
15 aqueous fluoropolymer dispersion contains hydrocarbon surfactant which causes said thermally induced discoloration.
4. The process of claim 3 wherein said aqueous fluoropolymer dispersion is polymerized in the presence of hydrocarbon surfactant.
5. The process of any of the preceding claims wherein said wet  
20 fluoropolymer resin is separated from said dispersion by coagulating fluoropolymer from the aqueous fluoropolymer dispersion and filtering to remove the aqueous medium.
6. The process of any of the preceding claims wherein said drying is carried out using drying gas heated to a temperature of about  
25 100°C to about 300°C.
7. The process of any of the preceding claims wherein said fluoropolymer resin is PTFE resin and said drying is carried out using drying gas heated to a temperature of about 100°C to about 200°C.
8. The process of any of the preceding claims wherein said  
30 fluoropolymer resin is melt-processible fluoropolymer resin and said drying is carried out said drying is carried out using drying gas heated to a temperature of about 160°C to a temperature about 10°C below the melting point of said fluoropolymer resin.

9. The process of any of the preceding claims wherein the fluoropolymer resin has an initial thermally induced discoloration value ( $L_i$ ) about 4 L units below the L value of equivalent fluoropolymer resin of commercial quality manufactured using ammonium perfluorooctanoate fluorosurfactant.

10. The process of any of the preceding claims further comprising pretreating the aqueous fluoropolymer dispersion.

11. The process of claim 10 wherein said pretreating the aqueous fluoropolymer dispersion comprises exposing the aqueous fluoropolymer dispersion to oxidizing agent.

12. The process of any of the preceding claims wherein said exposing of said wet fluoropolymer resin to an oxygen source during drying is carried out in the presence of alkali metal salt.

13. The process of claim 12 wherein said presence of alkali metal salt is provided by adding alkali metal salt to the aqueous dispersion medium prior to separating said wet fluoropolymer resin from said aqueous dispersion medium.

14. The process of any of the preceding claims wherein said oxygen source is selected from the group consisting of air, oxygen rich gas, or ozone containing gas.

15. The process of claim 14 where said oxygen source is ozone containing gas.

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2013/039394

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F8/06 C08F14/18 C08F2/16 C08F6/16 C08L27/12  
C08F6/22  
ADD. C08F14/26 C08F2/26 C08F2/30 C08L27/18 C08J3/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F C08L C08J B01J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 1 140 964 A (PECHINEY) 22 August 1957 (1957-08-22) claims; examples 1-8 page 1, left-hand column, paragraph 1 - right-hand column, paragraph 2 page 2, left-hand column, paragraph 2-3 -----	1-7,9, 12,14,15
X	US 3 700 627 A (MILLER HENRY C) 24 October 1972 (1972-10-24) claim column 1, lines 39-59 column 3, lines 7-10 column 4, lines 13-28 ----- -/-	1-4,7,9, 10,12-14



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/039394

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 380 605 A1 (ATOFINA [FR]) 14 January 2004 (2004-01-14) claims 1,16,17 paragraphs [0002], [0017] - [0022] paragraphs [0040] - [0044], [0046] - [0052]; table 1 -----	1-6, 8-11,14

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/039394

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